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Charging of a rodlike grain in plasma flow

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In present work on the basis of numerical modeling by the dynamics of many particles, a self-consistent problem of the formation of a charge accumulated by a dusty particle of a rodlike shape in a two-temperature plasma flow is considered. An analytical model useful for understanding the phenomenon of ion focusing and its effect on the formation of the surface charge of a needle was considered. Pairwise radial correlation functions evaluated in the approximation of binary interaction for moving particles with a stationary Coulomb center. Using conservation law for the momentum ion velocity component has been determined. It was noticed that electron shielding does not influence on the ion focusing density peak value. In that reason ion focusing parameters in the concrete doesn't depend on the electron screening Debye radius. A system with Coulomb particles containing moving point particles, ions and electrons, and fixed spheres have been chosen. The cases of dielectric and metallic dust grains having different orientations with respect to the flow direction are considered.

Key words: dusty plasma, ion flow, molecular dynamic, grain charge, drug force. PACS numbers: 51.50.+v; 51.10.+y; 52.80.Dy; 52.25.Fi.

1 Introduction

Dusty plasma is the object of intense experimental and theoretical research of recent years (see, for example, [1-4]). The present work continues a series of studies on numerical simulation of the properties of dusty plasma [5-11]. It investigated processes charging spherical dust particles and the structure of the space charge region around one dust particle placed in a single-temperature, twotemperature, resting [5, 7, 8] and moving plasma [6, 10, 11], as well as Brownian motion [7] and the dynamics of particulates in the plasma flow [6, 8]. In [9, 10], the mutual influence of the charging of two particles located along the flow and perpendicular to it is considered. In the present work, for the first time, the charge characteristics of a long-form dust particle have been investigated on the basis of a computational experiment, experiments with which are being actively carried out, and the theoretical study of their properties is very limited at the present time (see papers [12-15], in part the results of this paper are given in [11]). In the case of a supersonic ion plasma flow around a negatively charged spherical dust particle (such a situation can occur

when a dust particle levitates in the near-electrode plasma layer), a region of increased ionic densityion focus is formed behind the dust.

The process of formation, structure and characteristics of the ion focus are considered in [5, 6]. In the near-electrode layer, dust particles can form an ordered structure, and ion focusing can affect the interaction of particulates. To describe the interaction of particles in this case, it is not enough to use models based on the introduction of potential forces (the most commonly used is the screened Coulomb potential of Debye-Hückel). An example of this is the effect of ion focusing on the formation of the average charge of a particle in the wake tail considered in [9, 10]. The performed calculations showed that ion focusing on the first particle can lead to a significant decrease in the negative charge of the second particle due to the increased ion current. In this connection, the question arose about the effect of ion focusing on the charging of particles of an extended shape. In the present work, the formation of a space charge around extended-shape structures in a moving plasma is studied when the ion-focusing effect significantly affects the distribution of the space-charge region around the dust particle [11] and accordingly the density of the flux of charged plasma particles varies in different parts of the dust motif of the extended shape.

On the basis of a computational experiment, the charge characteristics of a chain of micron-sized dust particles (macroparticles) that touch each other and are placed in a plasma flow are investigated. Such a chain of dust particles simulates dust particles of extended shape. The cases of a different orientation of the needle relative to the flow are considered, and the dependence of the charge characteristics on the conductivity of the dust particle material is investigated.

2 Ion focusing in the binary ballistic approximation

Let us first consider an analytical model of ion focusing, which is useful for understanding the phenomenon of ion focusing and its effect on the formation of the surface charge of a needle. We obtain the necessary estimates in the same way as in [5], pairwise radial correlation functions were obtained in the binary interaction approximation of moving particles with a stationary Coulomb center. Let the stationary point Coulomb center (a massive dust particle) with a negative charge -Ze be placed at the origin of coordinates, onto which a uniform plane ion flux with density N_0 , mass *m*, positive charge *e*, velocity $V_{\infty} > 0$ flies from infinity. We select the x axis in the direction of the original ion velocity. Then, in the binary interaction approximation with a point Coulomb center, the ion moves in the collision plane along the trajectory described by the parametric equation [16]:

$$r = p / (1 + \varepsilon \cos \phi), \quad p = \rho_{\infty}^2 / \rho_{\perp},$$

$$\varepsilon = (1 + \rho_{\infty}^2 / \rho_{\perp}^2)^{1/2}, \quad \rho_{\perp} = e^2 Z / m V_{\infty}^2,$$
(1)

where *r* is the distance to the Coulomb center at some point of the trajectory, φ is the angle between the radius vectors at this point and the maximum approach point, V_{∞} is the velocity at infinity, ρ_{∞} is an impact parameter, *p* is the parameter, ε is the eccentricity of the collision [16]. It follows from (1) that an ion incident from infinity in the direction of the *x* with a velocity V_{∞} and impact parameter ρ_{∞} , intersects the *x* axis at some point $x_0(\rho_{\infty}) = \rho_{\infty}^2 / 2\rho_{\perp}$. The number of ions that intersect the *x* axis in unit time in the range $0 < x_0 < x$ $< x_0 < x_0 + \Delta x$, is $\Delta j = 2\pi N_i V_{\infty} \rho_{\perp} \Delta x$. The flux density per unit length of the *x* axis does not depend on the point on it.

The component of the ion velocity orthogonal to the *x* axis at the point of intersection of the *x* axis is determined by the momentum conservation law and is $V_{\rho}(x_0) = V_{\infty}\rho_{\infty} / x_0 = V_{\infty}(2\rho_{\perp} / x_0)^{1/2}$. From this it follows that near the axis x the density of ions is

$$N(x,\rho) = N_0 (2\rho_{\perp} x)^{1/2} / \rho.$$
 (2)

This expression, obtained for a collinear flow of non interacting ions, leads to an infinite value of the ion density on the axis. Interaction of plasma particles and thermal velocity spread leads to a blurring of the focusing peak near the *x* axis. Let us estimate the magnitude of the maximum ion density on the axis with allowance for the smearing due to the thermal velocity of ions $V_T = (T/m)^{1/2}$.

Let us assume that the thermal velocity of the ions is much less than the velocity of the directed flow. This condition is usually satisfied even for a subsonic flow because of the low ion temperature compared to the electron temperature. Then it is possible to average the density of ions over the radius determined by the thermal velocity of ions $\rho_0 = x V_T / V_\infty$.

The number of ions entering a thin cylinder around the *x* axis in the range $0 < x_0 < x < x_0 < x_{0+\Delta}$ *x* for a time τ is $\Delta N = \tau \Delta x J_x$, each of them will be in it for a time $\Delta t = 2\rho_0 / V_\rho$, the cylinder volume is $\Delta V = \pi \rho_0^2 \Delta x$, respectively, the average density in this cylinder $\langle N \rangle = \Delta N \Delta t / \Delta V \tau$. Hence we obtain the following estimate for the ion density near the *x* axis:

$$N_0(x) = N_0 (8\rho_{\perp} / x)^{1/2} V_{\infty} / V_T, \qquad (3)$$

which in the field of its applicability is in good agreement with the results of calculations of the ion focusing of a plasma flow around one and two macroparticles [6, 8, 9].

We note that electron shielding practically does not affect the value of the peak of the ion focusing density, so the parameters of ion focusing are practically independent of the electron Debye radius $r_{De} = (T_e / 4\pi N_e)^{1/2}$. A characteristic quantity that determines the parameters of ion focusing is the impact parameter $\rho_{\perp} = e^2 Z / m V_{\infty}^2$, at which the ion rotates after a flight near the particle to a right angle. The electronic Debye radius determines not the characteristics of ion focusing, but the scale of the length at which the space charge of the ion focus is screened. Screening by ions under conditions typical for dusty plasma, when $T_i \ll T_e$ and the thermal velocity of ions $V_T \ll V_{\infty}$, as well as electron shielding, does not play an important role in the formation of the ion focus. However, along with the size of the macroparticle, the Debye ion radius $r_{Di} = (T_i / 4\pi N_i)^{1/2}$ is the lower boundary of the region of applicability of formula (3). In the shielding of the charge of a macroparticle by ions, their contribution is approximately the same as that of electrons, since the characteristic kinetic energy of a directed ion flux is of the order of the electron temperature and, accordingly, the effective screening radius of ions roughly coincides with the electronic Debye radius.

3 Statement of the problem for numerical simulation

The technique used here to study the properties of a dusty plasma on the basis of the numerical integration of the equations of the dynamics of many particles is described in detail in [5–11]. This technique was adapted to solve the problem of the interaction of a plasma with a dust particle of an extended shape, the cylindrical dust particle was represented as a chain of spheres. If we assume that the charge of each sphere is uniformly along its surface, then the problem reduces to the usual scheme of solutions of the system of equations of motion of molecular dynamics. The errors of this model lead to a loss of information on the distribution of the charge density over a length equal to the radius of the dust particle. Because of this, near the surface of the speck, by reason of the averaging of the charge along its surface, the trajectories of ions and electrons will be inaccurately determined. In addition, some influence is exerted also by the geometric factor of replacement of a body of the cylindrical form, on a chain of spheres. Apparently, to calculate the charging characteristics, we should choose the dimensions of the spheres such that the volume of the cylinder and the total volume of the spheres coincide. But since at this stage of the study we are not talking about an accurate determination of the charging characteristics of a cylinder in plasma, but about the qualitative nature of the charge distribution of long-form dusty grains, the use of such a

model seems quite adequate to the purpose of the study.

We consider a system of Coulomb particles consisting of moving point particles, ions and electrons, and fixed spheres. Ions have a mass M, a positive charge e, electrons have a mass m and a negative charge -e. Let us consider the case when all spheres are fixed, have the same radius R, and absorb all the electrons and ions that fall on them. Accordingly, the charge of spheres is determined by the number of absorbed electrons and ions and depends on time. The case of Brownian motion of mobile spheres with variable mass and charge is considered in [7].

We consider the time evolution of a system initially consisting of 2n particles inside a parallelogram 0 < x < Lx, 0 < y < Ly, 0 < z < Lz. The trajectories of n positive and n negatively charged particles are determined by numerical solution of Newton's equations:

$$d^{2}r_{k} / dt^{2} = F_{k} / m_{k},$$

$$F_{k} = \sum_{l \neq k}^{2n+n_{g}} f_{kl}, \quad k = 1, 2, ..., 2n$$
(4)

here $r_k(t)$ is the radius vector of the κ - th particle, each of which is characterized by the mass m_k and the charge q_k , and n_g is the number of spheres. The Coulomb interaction force f_{kl} between mobile particles at distances between particles less than r_0 was modernized in accordance with the interaction of uniformly charged mutually permeable spheres of diameter r_0 . This value was chosen much less than the average interparticle distance and such that it did not influence the investigated characteristics. This was usually checked by comparing the results of calculations with various r_0 . When calculating the Coulomb interaction force f_{kl} between moving particles and spheres, it was assumed that the charge of each sphere is uniformly distributed over its surface.

The initial distribution of electrons and ions along the coordinates was chosen to be equiprobable in the volume of the calculated cell. The velocity distribution corresponded to the Maxwell-Boltzmann distribution at infinity. Depending on the initial distance to the nearest macroparticle, Maxwell's velocity distribution was shifted by the amount of interaction energy with the macroparticle. The direction of the velocity was chosen isotropic with a constant increment corresponding to the moving plasma. Thus, an initial distribution without bound particles (ions) was formed. In calculating flow characteristics, a sufficiently large initial time interval was emitted from consideration, on which the steady-state nature of the flow was established in the gasdynamic sense, and the values of dust charges reached the mean steady-state values.

The number of ions in the system was assumed to be fixed, the number of electrons was variable. The particle-throwing algorithm (instead of the absorbed ones) is used, which accurately preserves the neutrality of the entire system. Instead of the absorbed particle from a randomly chosen point on the surface of the calculated cell, the particles were thrown in such a way as to ensure the neutrality of the entire system, including the charge of the particulates. This procedure consisted in the fact that when the electron was absorbed, their number in the system decreased, and when an ion was absorbed, an electron-ion pair was injected into the system from a random point on the surface. Thus, the number of ions in the system was kept constant, while the number of electrons was variable, ensuring neutrality of the system.

The boundary conditions for modeling the ion flux differed somewhat from those used earlier [6, 8-11], where an absorbing condition was used for the ions at the right boundary and emitting on the left. Here, after the collision of the ion with the wall, it was thrown into the system from a random point on the surface. Moreover, the choice of a point on the surface corresponded to the fact that the distribution function of the particles entering the volume corresponded to the Maxwell distribution shifted by the velocity of the plasma flow. In the absence of absorbing spheres, this procedure yields a uniform plasma flow. When reflecting from the walls for electrons, thermostating boundary conditions were used. Thus, the Maxwell-Boltzmann distribution for electrons and the possibility of appearing in the simulated system of electrons having kinetic energy sufficient to overcome the potential barrier was maintained. This formulation of the problem allows us to take into account the charge and charge fluctuations of a macroparticle in a self-consistent manner.

In addition, a new realization of the boundary conditions makes it possible to simulate the flow of plasma around the dust particle at a lower ion flow rate more correctly than in previous studies, even when the flow velocity is comparable or even much lower than the thermal velocity of the ions. We note that the constant number of ions in the system, if it is possible to reduce the number of electrons due to absorption by a macroparticle, means that the average electron density in the modeled system can be significantly reduced in comparison with the ion density. An estimate of the decrease in electron density is the ratio of the charge of the macroparticle to the number of ions in the system. The situation, when the electron density in the cell is much lower than the ion density, corresponds to the case of dust clouds, crystals, in the near-electrode region the electron density is also lowered.

4 Results of numerical simulation

In all the above calculations, we studied a moving two-temperature argon plasma with z=1, a temperature of $T_i = 0.025 \ \mathfrak{sB}$ eV and electrons $T_e = 1 \ \mathrm{eV}$, the velocity of motion of the plasma corresponded to the kinetic energy of the ions $K_i = 1 \ \mathfrak{sB}$, $V_{\infty} = 2.2 \times 10^5 \ \mathrm{cm/s}$, thermal ion velocity $V_T = (T/m)^{1/2} = 2.4 \times 10^4 \ \mathrm{cm/s}$, ion density $N_i = 2 \times 10^{12} \ \mathrm{cm}^{-3}$. At $N_i = 2 \times 10^{12} \ \mathrm{cm}^{-3}$, the Debye radius (total) is 3.6 µm, the number of particles in the Debye sphere is 876. Plasma with such parameters is ideal for both ions and electrons. With the value of the charge of the needle Q/e = 3100, which is characteristic of the calculations given below, the impact parameter, at which the ion turns at a right angle, is equal to $\rho_{\perp} = e^2 Z / m V_{\infty}^2 = 2.2 \times 10^{-4} \ \mathrm{cm}$.

The calculated region was a parallelogram of size $20 \ \mu m \times 10 \ \mu m \times 10 \ \mu m$, in which 4000 ions were located. There were 6 spheres in the simulated volume, absorbing electrons and ions, touching each other and located along a straight line lying in the *xy* plane at $z = 5 \ \mu m$.

Fig. 1 illustrates three variants of the arrangement of spherical dust particles that touch each other and imitate a needle. The angle α characterizes the inclination of the needle relative to the ion flow. Variant a) corresponds to the location of the needle along the stream, the angle $\alpha = 0$, the coordinates of the sphere centers x = 5, 6, 7, 8, 9, 10 μm , y = z = 5 μm , with a radius $R = 0.5 \mu m$. Variant b) corresponds to the location of the needle at an angle $\alpha =$ $\pi/4$ to the direction of the ion flow, variant c) corresponds to the location of the axis of the needle perpendicular to the flow. The calculation time for these results was 26 ns, the ion Langmuir period was 21 ns. When calculating the average charging characteristics of the dust chain in the table and in the figures, the initial time relaxation region was ejected, which usually amounted to several ion Langmuir periods.

Table 1 – Integral charging characteristics of the entire chain of dust particles (calculations NeNe1-6), depending on the conductivity of the surface σs and the angle of inclination of the needle to the flux α . Calculation Ne7 is the characteristics of a single spherical speck of dust in the same flow. The time averages are given: the charge in electron charge units, the ion flux normalized to the unperturbed stream $J_0 = \pi R^2 N_i (2K_i / M)^{1/2}$, the average potential over surface φ_s , normalized to the electron temperature, the projections on the *x*, *y* axis of the dipole moment of the entire Coulomb system normalized by the quantity $P_0 = e N_i^{-1/3}$.

N⁰	σs	Angle	-Q/e	J/J ₀	-е ф s /Те	< P _x / P ₀ >	< P _y / P ₀ >
1	0	0	3157	125	3.08	9084	-118
2	0	π/4	3242	251	2.80	11090	1485
3	0	π/2	3199	187	2.80	11580	330
4	∞	0	3087	51	2.61	7301	3
5	∞	π/4	3159	246	2.74	10410	1165
6	∞	π/2	3220	192	2.83	11980	255
7	one	particle	1214	9	3.02	239	-10

In the table, the integral characteristics of the needles for different types of surface and the angle of inclination with respect to the flow are given, in addition, for comparison, the charging characteristics of one dust particle of the same size under similar conditions are included. In addition, the dipole moment of the entire system is calculated. Since the total charge of the system is zero, the magnitude of the dipole moment does not depend on the choice of the coordinate system – its projection to the x axis is equal to $P_x = \sum xq$, the summation is over all particles. The projection of the dipole moment onto the y axis is calculated in a similar way.



Figure 1 – Scheme of arrangement of a chain of dust particles (needle) relative to the ion flow: a) along the stream, the angle $\alpha = 0$, the coordinates of the sphere centers x = 5, 6, 7, 8, 9, 10 μ m, $y = z = 5 \,\mu$ m, with a radius $R = 0.5 \,\mu$ m; b) at an angle $\alpha = \pi/4$ to the direction of the ion flow; c) perpendicular to the flow

In Figure 2 shows the charging characteristics of dielectric dusty grains that do not conduct a charge and are located along the ion flow. Histograms are given that characterize: a) the value of the average negative charge of the speck of dust; b) the flux of ions per dust particle, normalized by a value $J_0 = \pi R^2 N_i (2K_i / M)^{1/2}$ that is equal to the gas-dynamic flow of cold ions absorbed by the sphere, moving in the same direction and having directional energy K_i ; c) the average surface potential of the dust particles, determined by all the plasma particles. When calculating the surface potential of a dusty grain, it was assumed that the charge along the surface of the dust particle was distributed uniformly.

In this case, the average potential over the surface from the sphere averaged over the surface of the other sphere is equal to the charge potential at the center of these spheres. In this case, a known property of the electrostatic potential is used, that its average value over the sphere is equal to its value at the center of the sphere (for a charge located outside the sphere). It is obvious that the error with this calculation of the average potential is very insignificant.

The results corresponding to this calculation are given in the first line of the table - calculation $N \ge 1$. The time-average charge of the entire needle, the ion flux absorbed by it, and the surface potential are presented. As the surface potential for the dielectric chain of dust particles, an average of 6 dusty grains is given. The table also presents the projections of the dipole moment of the entire system. Charging characteristics of dusts that do not conduct an electric charge and are located along the flow (calculation No1 from the table): a) the value of the average negative charge of the dust particle; b) the flux of ions per dust particle, normalized by the flow $J_0 = \pi R^2 N_i (2K_i / M)^{1/2}$; c) average surface potential of dust particles.



Figure 2 – Charging characteristics of dusts that do not conduct an electric charge and are located along the flow (calculation №1 from the table):
a) the value of the average negative charge of the dust particle;
b) the flux of ions per dust particle, normalized by the flow J₀ = πR²N_i(2K_i / M)^{1/2};
c) average surface potential of dust particles

In Figure 3 and 4 show the results of calculating the densities of ions and electrons around dielectric dust particles. In Figure 3 shows the ion densities in the *xy* plane passing through a chain of dust particles. Here and below, in all the figures, the values of the density are normalized to the mean ion density $N_i = 2 \times 10^{12} \text{ cm}^{-3}$. In Figure 3a shows the distributions of the ion density along the *x* axis at y = 0.1, 1, 2, 3, 4, 5 μm . The maximum ion density, which exceeds the average density by about 8 times, is reached immediately behind the dusty grain. The estimate from formula (3) gives for this point a density exceeding by about 16 times. Obviously, the difference is due to the influence of the fineness of the size of the dust particles (the shadow effect), the screening of the charge of the needle and the repulsion of the ions near the peak density. Obviously, all these factors lead to dissipation – the spreading of the peak density. In general, estimates (2) and (3) correctly describe the behavior of the density in the ion focus (wake tail). In Figure 3b shows lines of equal level in the *xy* plane passing through a chain of dust particles. In Fig. 3c shows a three-dimensional image of the ion density surface in the *xy* plane passing through a chain of dust particles. In Figure 4 shows similar distributions for the electron density.



Figure 3 – Density of ions in the xy plane passing through a chain of dielectric dusts:
a) the ion density distribution along the x axis at y = 0.1, 1, 2, 3, 4, 5 μm;
b) a line of equal level in the xy plane passing through a chain of dust particles;
three dimensional image of the ion density surface in the xy plane passing through a chain of dust particles;



Figure 4 – Similar to Figure 3 distribution for the electron density

In Figure 5 shows the characteristics for a charge-conducting needle oriented along the ion flow - calculation No. 4 in the table. Here are the histograms characterizing: a) the value of the average negative charge of a dusty grain; b) the flow of ions to the dust particle; c) the flow of electrons to the dust particle. The fluxes of ions and electrons to the dust particle, as in Figure 2 are normalized by magnitude J_0 . In contrast to the calculation of dielectric dust grains, the surface potential of metallic dusts does not change, because dust particles touch each other, but the fluxes of ions and electrons vary significantly. In Figure 5 a) circles with a thick dot in the center indicate the values of the equilibrium charge obtained from the simplest model of the charge distribution on metallic spheres placed not in the plasma but in vacuum. In this model, it was assumed that the total charge Q=3087e obtained in the calculation of No4 was redistributed over the spheres in such a way that the surface potentials of all the dust particles were equal. When calculating the surface potential of a dust particle, it was assumed that the charge along the surface of the dust particle is uniformly distributed, respectively, the average potential from other spheres is equal to the potential determined through the distances between their centers. In Figure 6 shows the charging characteristics of the needles located at angles $\alpha = \pi / 4$ and $\alpha = \pi / 4$ 2 to the flow - calculations N_{2} , 3, 5, 6 from the table. In Figure 6a) the values of the mean negative charge of dust particles are given; in Figure 6b) is the average surface potential of the dust particles.



Figure 5 – Charging characteristics of dust particles conducting electric charge and located along the flow (calculation №4 from the table):
a) the value of the average negative charge of the dust particle;
b) the flow of ions,
c) the flow of electrons to the dust particle, normalized to the flow



Figure 6 – Characteristics of charge of dust particles when the needle is placed at angles $\alpha = \pi/4$ and $\alpha = \pi/2$ to the flow - calculations No2, 3, 5, 6 from the table (circles, dots, dashed curves and solid curves, respectively): a) the value of the average negative charge of dust particles; b) the average surface potential of the dust particles

5 Discussion

The results of the calculations show two interesting new effects: the effect of ion focus on the character of charge of a long needle and a strong dependence on the conductivity of the surface of the dust particles. Strictly speaking, to ensure the equipotentiality of the surface, there is no need for the entire dust particle (its volume) to be conductive (metallic). The finite surface conductivity (even rather low) may be sufficient to ensure equipotentiality. Since the surface of the dust particles is exposed to particles of plasma and radiation, surface conductivity can also occur in dielectric materials. This possibility must be taken into account in interpreting the experiments.

Let us first consider the charging characteristics of the needles oriented along the ion flow. In this case, the total charge of dust particles for both types of surface differs insignificantly (for an insulator it is approximately 2% higher), but the nature of the distribution of charge density along a dusty grain varies radically. In a dielectric dusty grain, about half of the charge is concentrated at its beginning, and then there is an area in which the charge density even changes sign. This effect is due to focusing into this part of the dust particle a more significant ion flux and a corresponding decrease in the electron flux due to the geometric factor. As a result, the dielectric dusty grain has a significant dipole moment, which can have a significant effect on its stability and lead to the appearance of oscillations [13] and rotation [14].

Another interesting feature is that the flow of plasma particles to a dielectric dusty grain is approximately two and a half times higher than that of a metallic particle (with an approximately equal total charge – see table, calculations N (3). That is, the dielectric speck because of the accumulation of charge in its nose more strongly focuses the ion stream on its tail. Accordingly, a large drag force on the ion side, due to the momentum transfer during collision, acts on the dielectric dust particle.

Let us now consider the charging characteristics of the needles oriented at an angle to the direction of the ion flux. In this case, the total charge of the needles also differs insignificantly and practically does not depend on either the angle or the type of surface (see table, calculations $N \ge 2$, 3, 5, 6). The nature of the distribution of the charge density along the needle is the same for all calculations, see Fig. 6 a) and is close to the distribution of the charge density distribution of a conducting dust, located along the flow. Accordingly, for all these calculations, the distribution of the surface potential of the needles is also close.

An interesting feature is the appearance of a significant dipole moment in a direction perpendicular to the flow, with an acute "angle of attack" $\alpha = \pi / 4$. This effect, together with the dependence of the drag force on the angle, opens up rich possibilities for the appearance of rotational oscillations, a simple analytical model of which was considered in [14]. We note that an attempt has also been made in [15] to study theoretically the behavior of charged needles in an ion beam. But since it used the model of a very long needle and did not take into account the focusing of ions, the comparison of the results obtained there with the present calculations goes beyond the range of applicability of the theoretical model.

6 Conclusions

The results of numerical simulation lead to the need to rethink many phenomena observed in the near-electrode layer containing dust particles of extended shape. The inhomogeneity of their charging, the large dipole moment of the needle itself and the surrounding plasma (see the experimental results in [15]) lead to a very complex interaction of the needles between themselves and the surrounding plasma. Although the developed model is the first numerical experiment to investigate the electrical characteristics of spindle-shaped structures located in the ion flow of the near-electrode layer and, in spite of sufficiently significant assumptions embedded in the numerical model, the calculations make it possible to clarify the character of the charge formation of long-sized dust grains, to analyze the kinetic processes leading to formation of dust structures in the plasma, to test theoretical models [17 - 22]. These results are important for predicting processes under experimental conditions.

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Studies on gas release from pre-saturated samples on a plasma beam installation

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We conducted methodological studies to evaluate the possibility of conducting experiments on gas release from pre-saturated samples on a plasma-beam installation. One of the tasks of obtaining reliable data on the parameters of the interaction of hydrogen isotope ions with materials of the NNR is to conduct methodically correct post-test experiments on the study of gas release from the investigated samples subjected to ion irradiation. The paper presents three stages of research. In the first stage, experiments were conducted on saturation and gas release with the sample from tungsten. At the second stage, experiments were performed with a tungsten sample on saturation with its deuterium and degassing under stepwise heating conditions. At the third stage, experiments were conducted on gas release with vanadium samples, with maximum sensitivity for dissolved gas in the sample. The results of calculations of the temperature field on the sample are presented. It is shown that, on the whole, it reflects the experimentally observed effect on a significant sample temperature gradient.

Key words: tungsten, degassing, vanadium, plasma, temperature gradient, saturation, deuterium. PACS numbers: 85.40.Ry; 82.56.Lz; 82.30.Rs; 88.85.mh; 28.52.-s.

1 Introduction

Main points which impact on received data quality were defined for different research methods of gas release from samples after ionic radiation. Brief list of them:

A) Sample pre saturation should be conducted under controlled conditions, i.e. should have adequate information on main radiation parameters:

• geometry of irradiation;

• ion flux parameter data (ion flux density, energy spectrum of ion flux);

• temperature field data in the volume of irradiation sample during radiation;

• data on irradiation time.

B) Procedures of post irradiated sample preparation on gas release should be optimal from the aspect of obtaining highest adequate information on gas release experiments. Following aspects are important according to numerous studies:

• time of sample aging after irradiation, before gas release experiments should be possibly minimal;

• irradiated sample contact with atmospheric gas was not desirable.

C) Gas release experiments of irradiated samples should be conducted under conditions permitting to define correctly gas flow from researched sample and depending on its temperature.

It is obviously, that for effective research on defining parameter of plasma impact on fusion reactor material sample it is desirable to have method conduction of gas release experiments directly after irradiation on the same installation on which irradiation was conducted.

2 Material and methods

2.1 Experiments with tungsten samples

Researches were conducted on plasma beam installation (scheme is in Figure 1) using target cooling device in which different researched samples were set.

Following tasks were solved during the experiment:

1) determining of sample temperature at different places, for different heating modes of samples by electron and ion beam;

2) estimation of installation system operation impact on registration of mass-spectrometer data;

3) estimation of background gas release into an installation chamber for different heating modes of samples under continuous pumping conditions;

4) obtaining depending on gas release of dissolved hydrogen from vanadium sample under sample stage heating by electron beam;

5) receiving of gas release depending saturated from deuterium ion flux from vanadium sample under sample stage heating by electron beam.

Experiments with tungsten samples were primarily conducted, for which mode parameters of

sample temperature heating dimensions of 10 mm diameter; 4.5 mm thickness were estimated; data on composition of gaseous phase in interaction chamber for different stages of operation set of plasma beam installation under maximal pumping of chamber mode were given; experiments on saturation of tungsten sample by deuterium were carried out and gas release experiment under stage heating conditions was conducted.

Tungsten sample was chosen due to its properties. It follows from the literature sources (see Figure 2) on dissolution of hydrogen isotopes in given material (equally with molybdenum and other refractory metals and melts), that given material has one of the lowest volume in dissolution constant (less than in stainless steel for more than 2 order of magnitude).



Figure1 – Structural layout of plasma beam installation of simulation bench

Therefore, saturation and gas release experiments with researched sample from tungsten modeled in great amount condition impact of irradiated experiment on hydrogen isotope and target materials interaction, but not samples, defining lower border of possible background impact on such interaction.

Tungsten sample with 10 mm diameter and 4.5 mm thickness was set into target unit by molybdenum holder. CA typed thermocouple was set on sample reverse side.

Initially depending on gas composition changing in interaction chamber on serial turning on of all installation systems were taken: from cooling supply in electron beam gun chamber; back heating in cathode-breaker assembly; tablets; electro-magnetic system turning on; and creating heat up sample of electron beam by accelerating voltage changing for different values of sample acceleration voltages and currents. Experiments were conducted on scanning electron beam with 3 mm diameter on sample center, and on electron beam defocusing up to 30 mm diameter.

Main received experiment parameters were given in Table 1 and Figures 3, 4.



Figure 2 – Temperature depending of hydrogen solution in tungsten [4-7]

Table 1 –	Experiment	data on	heating o	f tungsten	sample

Temperature on sample front side, C	Temperature on sample reverse side, C	Pressure in chamber with electron gun; *10 ⁻⁶ , Torr	Pressure in interaction chamber *10 ⁻⁶ , Torr	Accelerating voltage, V	Current on sample, mA			
		Electron beam d	iameter of 3 mm					
	396	2.62	1.67	1000	12			
866	521	2.67	2.21	1200	15			
980	579	2.68	2.58	1400	16			
1026	596	2.71	2.11	1600	19			
992	583	2.67	1.61	1400	17			
848	510	2.64	1.23	1200	14			
-	414	2.65	1.07	1000	12			
975	576	2.63	1.3	1400	17			
Electron beam diameter of 30 mm								
	440	2.63	1.18	1400	17			



Figure 3 – Typical gas spectrum in interaction chamber under tungsten sample heating by electron beam



Figure 4 – Change depending of gaseous phase composition in interaction chamber under stage heating of tungsten sample by electron beam

Conclusions on experiment first stage with tungsten samples include the following:

1) Main peaks, observed for interaction chamber on mass-spectrometer are water (M18), nitrogen and carbon monoxide (CO) (M28) and hydrogen peaks;

2) Water peak (characterized for spectrum of residual gas of vacuum chamber, not exposed to burn-in) which is gradually decreased on chamber pumping, but is increased during target unit heating, by demonstrating peak release. Minor increase of hydrogen and carbon monoxide peaks are also observed under heating, which connects with gas release upon sample and target unit heating;

3) Nevertheless, general level of residual gas is not enough high (on hydrogen is less than $2*10^{-9}$ Torr for any heating mode) and permit to conduct gas release experiments;

4) different sample temperatures with accuracy of about 10 °C can be effectively set by accelerating voltage of electron beam heating sample;

5) there is marked temperature gradient through sample thickness of about 300 °C for front surface sample begin with 850 °C and above;

6) Electron beam defocussing leads to significant decrease of sample temperature more than 200 °C for same values of accelerating voltages.

Experiments on tungsten sample saturation with deuterium and degasification under the stage heating conditions by electron beam were conducted on the second stage of the experiment.

Experiments on saturation above all should allow to estimate sample temperature level during its heating by ion and electron beam. The main experimental parameters obtained are given in Table 2.

Saturation was conducted under deuterium pressure in recharging chamber about $3-5 \cdot 10^{-3}$ Torr; 500 V potential was given to sample upon saturation. Average saturation time was about 5 minutes on every temperature shelves.

Directly after saturation, interaction chamber was pumped from deuterium and gas release experiment was conducted.

Sample was heated initially by 30 mm diameter electron beam, then by 8 mm diameter electron beam. Mass-spectrum changes were registered, in particular peak changes corresponding to HD, deuterium hydrogen and water molecules. (see Figure 5).

Conclusions on the second stage of tungsten sample include the following:

1) deuterium release flow from tungsten sample could not fixed predictably after plasma impact on its subsequent heating; deuterium release from other target unit elements was also not fixed correspondingly, which allows to conclude that deuterium background level in chamber will not exceed 10⁻⁹ Torr for gas release experiments

2) different sample temperatures with accuracy of about 10 °C under its saturation from plasma discharge can be effectively set by accelerating voltage of electron beam heating sample 3) there is marked temperature gradient through sample thickness under its saturation of plasma flow which consists 300 °C for front surface sample begin with 850 °C and above.

Therefore, preliminary stage of methodic experiments was finished which leads to obtain approach to conduct method on gas release experiments on plasma beam installation, number of parameters relate to temperature fields on sample volume under its saturation and degasification conditions, electron beam parameters providing necessary temperature samples were received, background values of gas composition in chamber with sample during conducting gas release experiments were estimated for researching saturation/degasification mode.

Table 2 –	Test data	on tungsten	sample sa	aturation b	y deuterium
		<u> </u>			-

Temperature on sample front side, C	Temperature on sample reverse side, C	Pressure in chamber with electron gun; *10 ⁻ ⁶ , Torr	Accelerating voltage, V	Current on a target, мА	Current on sample, mA				
	Electron beam diameter of 30 mm								
	141	2.5	1900	62	28				
	209	2.7	2200	78	32				
		Electron beam d	iameter of 8 mm						
	312	2.63	1500	41	19				
	460	2.4	1900	59	26				
835	530	2.4	2000	74	28				
878	546	2.6	2200	78	30				



Figure 5 – Depending of gas phase composition change in interaction chamber under stage heating of tungsten sample after plasma impact

2.2 Experiments with vanadium samples.

Experiments with vanadium samples were conducted on the second stage: first sample was similar to tungsten sample (dimensions of 10 mm diameter, 4.5 mm thickness); second sample was thinner (dimensions of 10 mm diameter, 2 mm thickness). Purpose of experiments was to define experiment mode parameters on gas release of preliminary saturated samples with maximal sensitivity of dissolved gas in sample.

Vanadium sample material was chosen for these purposes. Vanadium has high parameter values of hydrogen isotope dissolution (Table 3). Hydrogen dissolution in vanadium is more than 7 order of magnitude high, in comparison with tungsten. Being hydride-forming material, vanadium is capable to

absorb water in significant amount – volume hydrogen concentration in vanadium hydride exceeds hydrogen concentration in liquefied condition. In addition, relatively small hydrogen concentration is presented in it. All this together makes it convenient material for saturation and gas release experiments.

Source	Isotope	So (at. fraction Pa ^{1/2})	Es (meV)
[8] 120-470 °C	Н	2.2E-6	-331
[9] 220-550 °C	Н	1.6E-6	-353
[10] 600-1200 °C	Н	3.6E-6	-293
[11] 20-150 °C	Н	1.7E-6	-344
[12] 200-450 °C	Н	2.1E-6	-330
[13] 700-1200 °C	Н	1.7E-6	-344
[14] 30-700 °C	H D T	2.4E-6 1.9E-6 1.6E-6	-331 -341 -358

Table ?	2_	Parameters	ofh	vdrogen	isotones	dissolut	ion in	vanadium
I able .) —	rarameters	01 II	yulogen	isotopes	uissoiut	юн ш	vallaululli

Experiments with first vanadium sample concluded on following: after sample installation water was pumped and sample was heated in stages by electron beam. Experiments were conducted under different beam parameters and different modes of interaction chamber pumping. Mode with one TMP pumping was mainly used which is set on massspectrometer for increasing system sensitivity of mass-spectrometer registration. Changes of gas composition in chamber were registered during experiments.

One of the first stage heating samples allows fixing significant release of dissolved hydrogen in vanadium sample (see Figure 6). Hydrogen release character completely corresponds to expect one: on first electron beam supply by accelerating voltage about 1000 V on sample it begins slowly heated and we observe pressure peak and growth of released hydrogen at initial time depending on sample warmup. Further on increasing of accelerating voltage up to 1400 V, great peak of hydrogen release was observed which declines with time (temperature balance set is more faster than on the first warm-up as sample temperature is significantly higher); and on last accelerating voltage increase there was observed last hydrogen peak which is less than previous (as hydrogen basic amount is already released from sample probably). At the expense of diffusion speed increase with sample temperature hydrogen release decay for second peak is more "fast".

It should be noted there, that obtained experiment results on vanadium sample degasification, carried out on high sensitivity of registration system were completely approved principal possibility of gas release experiment conduction on plasma-beam installation.

Experiments with second vanadium samples were conducted for further task on defining optimal gas release method on plasma-beam installation. Second researched sample was thinner than the first, by reason of increasing method correctness:

1) for temperature and concentration gradient reduction on sample under its saturation in ion flux and warm-up by electron beam;

2) for reduction of temperature balance occurrence on sample upon its saturation in ion flux on electron beam warm-up;

3) for more correct processing of obtained gas release depending, here we have to clarify that mathematical apparatus of atom migration was well developed in present, ratio of average linear dimension (in this case diameter) to sample thickness, in which is no more than 4. In other cases, gas release depending processing should conducted by special design/model programs.

After second vanadium sample installation, its stage annealing was conducted under continuous pumping and mass-spectrometer registration conditions. Figure 7 shows depending change of hydrogen pressure in chamber during annealing. As can be seen from figure, hydrogen release depending similar to previous obtained one. It is seen, that at the annealing end, the sample was degasified from dissolved in it hydrogen.

Saturation of vanadium sample by deuterium was conducted after annealing. Saturation was conducted in 30 minutes under deuterium pressure in chamber of 5*10⁻³ Torr on sample temperature of about 160 °C. Electron beam was on defocussing mode (diameter of 30 mm); accelerating voltage of 1400 V; beam current of 16 mA; current on a target of 58 mA. Potential of 1000 V was given to a target unit.

Further experiment on deuterium gas release from saturated vanadium sample was conducted. Experiment diagram is shown in Figure 8. It is seen that experiment allowed to obtain qualitative gas release kinetics of deuterium and HD molecules. It turned out that deuterium quantity entered in sample in the result of interaction with ion flux was about $3*10^{-6}$ mol.



Figure 6 – Depending of gas phase composition change in interaction chamber under stage heating of vanadium sample



Figure 7 – Change depending of hydrogen partial pressure in interaction chamber on vanadium sample stage heating



Figure 8 – Gas release depending of hydrogen isotopes on stage heating of preliminary saturated vanadium sample

3 Results and discussion

Gas release depending analysis on stage heating. Analysis of deuterium gas release depending from vanadium sample was conducted within the assumption of release diffusion mode predominance and based on known approaches to solution of onedimensional diffusion equation.

It is known that, Fick's equations are main equations described hydrogen mass transfer in metals. They are written as follows for onedimensional case:

$$J(x,t) = -D(t)\frac{\partial C(x,t)}{\partial x}$$

$$(1)$$

$$\frac{\partial C(x,t)}{\partial t} = D(t)\frac{\partial^2 C(x,t)}{\partial x^2}$$

First equation describes gas penetration rate through environment surface unit. Second equation determines hydrogen accumulation at certain point of environment as function of time *t*.

Depending on conditions at interface gas is solid x=0, x=1, equation (1) is Cauchy problem with different boundary conditions.

First order boundary conditions. In this case is generally believed that the concentration at boundary layers is equal to equilibrium solubility. Then for diatomic gas:

$$C_{0}|_{t\geq0} = \Gamma \sqrt{P_{0}} , x=0$$

$$C_{l}|_{t\geq0} = \Gamma \sqrt{P_{0}} , x=l$$

$$(2)$$

where $\Gamma = \Gamma_0 exp (-H_s/RT)$ – solubility, referred to pressure unit, P_0 and P_l – hydrogen pressure on boundaries (on membrane inlet and outlet sides, as an example). Physically, first order boundary conditions mean that interphase process rate is extremely great in comparison with diffusion mass transfer rate.

Second order boundary conditions are set through diffusant flow at membrane inlet and outlet, equal to constant value:

$$-D \frac{dC}{dx} = J_0, x=0$$

$$. \qquad (3)$$

$$-D \frac{dC}{dx} = J_1, x=l$$

On third order boundary conditions, hydrogen concentration at membrane boundary layers is set as flow function through membrane and pressure in gaseous phase. Third order boundary conditions are divided into linear and non-linear relate to hydrogen concentration. Linear transient-free boundary conditions allow to analytically solving transient diffusion problem.

$$K_{H}P_{0} - K_{D}C_{0}(t) = J_{0}(t) , x=0$$

$$, \qquad (4)$$

$$-K_{H}P_{l} + K_{D}C_{l}(t) = J_{l}(t) , x=l$$

where K_H and K_D - generalized constants of saturation and degasification relatively. For more correct process description, due to associative character of desorption, non-linear transient third order boundary conditions should be used, considering degasification rate as proportional to C^2 . Then boundary conditions could be written as equation system, describing flow balance on membrane surface and boundary layers:

$$s\mu p - bN_0^2 - \rho N_0 + \eta C_0 = 0 , x=0 , \qquad (5)$$

$$\eta C_l - \rho N_l - bN_l^2 = 0 , x=l$$

where ρ – constant of hydrogen transfer from adsorbed to absorbed state, η - constant of hydrogen

atom outlet rate from volume to surface, s – hydrogen adhesion coefficient, equal to the ratio of the adsorbed particle number to the total number of falling particles on gaseous phase surface, μ – gaskinetic coefficient, equal to molecule numbers, falling on surface unit in time unit on single hydrogen pressure, b – constant of desorption rate, N_o and N_l – adsorbed atom concentration at membrane inlet and outlet surfaces.

There is not analytical solution of transient-free diffusion problem on third order boundary conditions.

It is generally assumed that, gas release occurred by diffusion or by first and second order desorption. Gas release process at diffusion mode is described by Fick's equations at classical diffusions or by diffusion equations in defective environment.

For estimation and comparison of obtained kinetics of hydrogen release there can be assumed that deuterium release in above mentioned experiment is determined by diffusion processes (even if it is not such, anyway obtained diffusion coefficient has diffusion effective coefficient meaning and can be characterize kinetic process).

Under boundary conditions $C(0,t) = C_1, C(H,t) = C_2$ and initial concentration distribution C(x, 0) general solution of diffusion equation in the region of finite sizes is given by the equation:

$$C(x,t) = C_1 + (C_2 - C_1)\frac{x}{H} + \frac{2}{\pi}\sum_{n=1}^{\infty} \frac{C_2 \cos n\pi - C_1}{n} \sin \frac{n\pi x}{H} \exp\left(-\frac{n^2 \pi^2 D t}{H^2}\right) + \frac{2}{H}\sum_{m=0}^{\infty} \sin \frac{n\pi x}{H} \exp\left(-\frac{n^2 \pi^2 D t}{H^2}\right) \int_0^H C(\xi,0) \sin \frac{m\pi}{H} \xi d\xi$$
(6)

For considered at our experiment desorption case, under continuous pumping conditions it replied to the following boundary and initial conditions: C(x, 0) = f(x), C(0, t) = 0, C(H, t) = 0. Then equation on hydrogen concentration account will be following:

$$C(x,t) = \frac{2}{H} \sum_{m=0}^{\infty} e^{-\frac{\mu_m^2 D t}{H^2}} \int_0^H C(\xi,0) \sin\frac{m\pi}{H} \xi d\xi$$
(7)

where $\mu_m = m\pi$.

If assume that hydrogen is equal distributed on sample, then there could be another simplification by

setting initial condition as: $C(x, 0) = C_0$. Then concentration profile will be determined as follows:

$$C(x,t) = \frac{4}{\pi} C_0 \sum_{k=0}^{\infty} \frac{1}{2k+1} e^{-\frac{(2k+1)^2 \pi^2 Dt}{H^2}} \cdot \sin \frac{(2k+1)\pi}{H} x$$
(8)

Considering that diffusion coefficient (see Figure 9) has Arrhenius temperature depending there can be conducted the variation of pre-exponential factors and diffusion activation energy for modeling of obtained gas release depending by recurring:

$$D = D_0 \exp(-\frac{E_d}{RT}) \tag{9}$$

Here D_0 – pre-exponential factor of diffusion coefficient, E_d – diffusion activation energy, R – universal gas constant, T – temperature.



Figure 9 – Diffusion from finite bodies with joint borders (desorption from plates)

It should be noted separately, that 2 decay curves of diffusant flow from samples obtained at a different temperature is necessary for modeling. Then first peak computing will be for temperature values T1 by equation (8), and for second peak of temperature values T2 by equation (7) where initial condition will be defined as C(x, 0) = C(x, t1); t1 – changing time of sample temperatures from T1 to T2.

This computation and variation was conducted for experiment on deuterium release from vanadium sample. (Modeling data of deuterium flow decay on sample temperature of 500 °C is given in Figure 10).

Obtained Arrhenius depending of deuterium diffusion of effective coefficient: $D(T)=(5\pm1)*$ $10^{-8}*exp((12530\pm1000)/(R*T))$ coincide on volume order with number of literature sources [15-21].

However we believe that, it is more appropriate for distribution modeling of hydrogen isotope concentration on sample at all experiment stages on saturation/release, to conduct by modern software platforms. COMSOL Multiphysics environment was considered at level of estimation possibility of such modeling.

Potentially, it allows to join two tasks: diffusion and thermal balance in a three-dimensional body (at researched sample) and get temporary distribution depending of sample temperature and hydrogen concentration in sample.

At the present stage of development of experiment analysis means on saturation and gas release, in the basis of COMSOL Multiphysics software environment, thermophysical computations of temperature field distribution on sample during impacting electron beam on its surface.

Transient heat transfer model was used during computation of considering case of radial heat:

$$\rho C \frac{\partial T}{\partial t} + \nabla q = \mathbf{Q}; \ q = -k \nabla T; \tag{10}$$

where ρ – thermal conductivity material density (environment); *C* – material thermal capacitance; *T* – temperature; *q* – heat flow; *k* – thermal conductivity coefficient; Q – heat source; ∇ – divergence operator(vector).



Figure 10 – Results of modeling deuterium release from vanadium sample at a sample temperature of 500 °C

Design model geometry was given in Figure 11 A. Disc type sample from 10 mm diameter and 2 mm thickness vanadium was given in the form of half section on axis Z. Sample heating was conducted by supplying thermal energy to sample upper surface: all surface of sample was heated. Outer side of disc circle is cooled by water at the temperature of 50°C. Outer and lower surface of discs radiate thermal energy by the law $q = -\varepsilon\sigma(T_o^4 - T^4)$, where ε -material emissivity; σ -Stefan-Boltzmann constant, T_0 - environment temperature (installation), is equal to 50°C. Further power of sample radial heat was set for computation in W/mm².

Three-dimensional space grid sample on the basis of two-dimensional axially symmetric geometry was built for numerical modeling, example of «B SCHEME» which is given in Figure 11 B.

Computation results of temperature field on sample were given in Figures 12, 13. It is shown that generally it reflects experimentally observing effect on sample thickness significant temperature gradient.



Figure 11 – Sample geometry and calculation model



Figure 12 – Temperature field on vanadium sample after 5 sec heating. Beam power is 5 W/mm²

4 Conclusions

Main conclusions on conducted experiments will be following:

1) Possibility of conduction gas release experiments of preliminary irradiated samples on plasma-beam installation was approved and demonstrated; main procedures of such test conduction were determined; methods to analysis and development of saturation/gas release experiment results were introduced.

2) Absorbed deuterium atom quantity at ion radiation time and effective coefficient of deuterium



Figure 13 – Temperature field on vanadium sample after 5 sec heating. Beam power is 5 W/mm²

diffusion in vanadium were detected according data on methodical saturation/gas release experiments with vanadium sample.

3) Technical requirements on gas release experimental conditions, and to its procedure conduction as follows:

• hydrogen isotope quantity in researched saturated sample should be less than $3*10^{-10}$ mol;

• sample should be more than 2 mm thick;

• sample should be annealed up to temperature of 100 °C more than assumed temperature at gas release experiments, before saturation experiment conduction • registration of temperature on sample front and reverse side within the range of 500-1000 °C is necessary during experiment conduction.

• gas release experiments are necessary to conduct at no less than 2 different temperatures (preferable at temperatures of 500 °C and 1000 °C)

• time between sample saturation and its degasification should be no less than 10 minutes for decreasing of background gas pressure in interaction chamber;

• sample warm-up by electron beam is necessary to conduct under beam defocusing conditions at all sample surface

• mass-spectrum registration should be conducted at turning on SEM within the range of mass number 2 up to mass number 28, with rate of not less than 1 mass-spectrum in 25 seconds.

4) Important tasks were formulated, solution of which could significantly improve quality of integral material testing researches on plasma-beam installation. That important tasks are as follows: • Conduction of the experiments on calibration of mass-spectrometer system of plasma-beam installation for different gas and different installation pumping configuration;

• Development and test conduction on defining ion beam parameters;

• Making a system of sample line heating by electron beam, for the purpose of realization of tests on sample thermal desorption in line heating mode;

• Development and making method of analysis and modeling experiment results on sample saturation/degasification on plasma-beam installation with COMSOL Multiphysics software platform.

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Temperature-dependent quantum pair potentials and ionization in Helium-like plasmas

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Diffraction corrected effective and Coulombic electron-ion interaction are worked out for helium like ions in plasmas of warm dense matter (WDM) and chemically-reacting concern, through explicit wave functions derived within an appropriate quantum defect framework. Very significant departures from the usual and corresponding hydrogenlike expressions are then witnessed. To do so, we strongly rely on a coherent quantum defect model (QDM) making use of parameters qualifying departures from hydrogenic bound states with same quantum numbers for negative energies as well as phase shift corrections for positive energy levels. Such an approach is also completed with a very accurate Hartree-Fock (HF) approximation for the ground state. The QDM then approaches the Slater sum-over-state- for the binary electron-ion where the pertaining ion retains an electron on its 1s hydrogenlike ground state. The resulting electron-ion effective interactions are then analytically derived through classical pair correlation functions. These latter are thoroughly contrasted to their hydrogenlike homologues. In addition,ionization in a 3-component electron-two ion system is also given a certain attention.

Key words: Helium-like ions, diffraction pseudopotentials, warm dense matter, ionization. PACS numbers: 52.27.Cm,52.70.-m; 31.10.+z; 52.25.Jm.

1 Introduction

To deal efficiently with basic and statistical physics concepts of central concern in dense and partially ionized plasmas, one is often confronted to the pitfall arising from the short range divergence of the ubiquitous electron-ion attraction [1-9]. A straightforward and pertinent approach allowing to circumvent this difficulty while maintaining a quasiclassical setting for equilibrium and transport properties is the mitigation at high temperature $(T \ge 1 \text{ Ry for low Z ions})$ of the given attraction diffraction corrections due to through the uncertainty principle. Up to now this standard procedure remains restricted to hydrogen-like electron ion interactions. This situation is mostly due to the identification of Gibbs potential with corresponding Slater sum requiring explicit wave function for the given pair of unlike charges. Moreover, when one is confronted to heavy ions (Z>>1) retaining many bound planetary electrons, a Thomas-Fermi like description [10] is then usually in order, thus avoiding the use of explicit wave functions. However, strong and persistent request, mostly from the warm dense matter (WDM) community [11-12] stressing strongly coupled plasmas with solid density and $T(eV) \le 10$, as well as accurate diagnostics of ion-plasma interaction [13,14], put a recent and urgent emphasis on Helium like ions, i.e. with nuclei (any Z) retaining a strongly bound ls electron.

Accurate analysis of equilibrium and transport properties of helium-like chemically reacting plasmas [15] also features a significant domain of present concern where He-like Coulomb-like interactions are also urgently requested. In order to appreciate the present Slater sum approach within the perspective afforded by the present very active field of simulation techniques dedicated to WDM investigations based on path integral Monte-Carlo (PIMC) methods or on the extraction of ion-ion effective interactions [16-19] from N-body quasiclassical approaches, one witnesses an urgent demand for accurate non hydrogenic electron-ion pseudopotentials. In particular, the matching of PIMC thermodynamics at high temperature with the Debye one [16] requires that partial ionization and ion excitation be carefully accounted for temperature higher than the helium-like ion ionization energy (Eq.(27) in the sequel).

In this report, we intend to demonstrate an analytic derivation of the pertaining electron- ion pseudopotential, for this specific 3-body problem. Toward this goal we systematically rely on a consistent quantum defect model (QDM) [20, 32] based on parameters a_b qualifying departures from hydrogenic bound states energies and a_c for the phase shifts of the positive energy levels. Such an approach, completed with a HF ground state description [23] is validated by its overwhelming success in reproducing helium atom properties as quantitatively accurate as the hydrogen atom ones.

The present work is thus structured as follows. Sec. 2 develops the quantum defect model (QDM) approach to the Slater Sum-over- states for the binary system electron-ion $Z_1(Z_1=Z-1)$, with ion Z_1 kept on its hydrogenic 1s ground state. Concommittent spin effects are also paid a due attention. The given temperature-dependent e-ion Z_1 effective interactions are then analytically detailed in Sec. 3, through the corresponding pair correlation function. The novel helium-like pseudopotentials are systematically contrasted to their hydrogen-like homologues, taken in a sequence with increasing precision. Ionization ion in a 3-component e-ion Zion Z_1 dense plasma is worked out in Sec. 4, with the aid of canonical free energy including electron exchange as well as quantum corrections featuring QDM parameters for e-ion Z₁ excited states. The following analysis implies that the plasma electrons remain classical (non degenerate), thus keeping their Debye length larger than the de-Broglie thermal one and still smaller than their average interdistance.

2 Slater sum approach (SSA)

2.1. Bound state contributions

Our basic concern is the plasma electron-ion effective interaction (pseudo-potentiel) in a He-like plasma where most of the ions (nonrelativistic) have the charge Z_1 =Z-1, i.e. retain a strongly 1s bound orbital electron. As in the well-known H-like the searched pseudopotential writes as (β = 1/k_{β}T)

$$U(r) = -\frac{1}{\beta} \ln[g(r)]$$
(1)

in terms of the $e-Z_1$ ion canonical correlation function. The main focus of the present work is to

demonstrate a complete calculation of g(r) based on the present knowledge of the He atom physics. Numerically speaking, the latter is presently as accurate as the H atom one [20]. In order to make our derivation of present e-Z₁ effective interaction as close as possible as to its Hydrogen like homologue with ion of charge Z, we shall elaborate our further developments on the quantum defect method [20]. Such an approach should secure an immediate matching with hydrogen-like (non relativistic) wave functions of the present QDM ones. Then, the corresponding 2-body and bound state part of g(r) appears under the H-like form (β =(1/k_{\beta}T)[•]

$$g_{L}(r) = \frac{1}{4\pi} \left(\frac{2\pi\beta \hbar^{2}}{m} \right)^{3/2} \sum_{n=1}^{\infty} \sum_{\ell=0}^{n-1} (2\ell+1) \times \exp(-\beta E_{n\ell}) |R_{n\ell}(r)|^{2}$$
(2)

in terms of (n, ℓ) H-like excited states (m is the electron mass) with energy E_{nl} and wave-function $R_{nl}(r)$ derived from their H-homologues though the QDM procedure detailed below. The first term n = 1, $\ell = 0$ pertaining to ground state is given a specific Hartree-Fock attention with the parametrized expression,

$$\frac{1}{2Z_1^{3/2}}R_F(r) = \sum_{i=0}^2 c_i \left(\frac{k_i}{Z_1}\right)^{3/2} \exp(-k_i r) \quad (3)$$

by Clementi and Roetti [23]. Some excerpts of the required parameters tabulations are given on Table 1.

The corresponding $g_L(r)$ contribution is adequately parametrized with $\xi = \frac{L}{\lambda} = Z_1 \beta^{1/2}$, ratio of classical Landau length to the De Broglie electron wavelength. So, with $x = \frac{r}{\lambda}$, the HF partial correlation featuring the fundamental He-like state writes as

$$g_F(x) = 2\sqrt{2\pi}\xi^3 \exp(\xi^2 \varepsilon^*) *$$

$$* \left[\sum_{i=0}^2 c_i \kappa_i^{*3/2} \exp(-\xi \kappa_i^* x) \right]^2$$
(4)

where $\kappa_i^* = \kappa_i / Z_1$ et $\epsilon^* = \epsilon / Z_1$

Z	k ₀	kı	k2	C0	c 1	C 2	z(a.u.)
2	1.45286	2.77954	4.34600	.82958	.18334	.00824	.91795
3	2.45055	4.57259	6.67032	.89066	.12328	.00088	2.79226
4	3.43071	5.63150	7.35143	.89855	.09068	.02158	5.66712
5	4.44422	74.90274	11.31380	.93036	.07786	.00013	9.54194
6	5.44726	9.80425	14.61460	.94428	.06382	00125	14.41690
7	6.45215	11.69880	19.74410	.95445	.05228	00096	20.29181
8	7.45601	13.66210	22.59050	.96175	.01115	00121	27.16675
26	25.45370	47.42210	56.67690	.98817	.01692	00361	321.91659

Table 1 – Hartree-Fock coefficients and ionization energies for the He-like sequence. (Clementi-Roetti[23]) $\Phi(r) = 2\sum_{i=0}^{2} c_i k_i^{3/2} e^{-k_i r}$

Next, we have the n, ℓ) excited states, which we intentionally limit to ℓ =0,1 and 2 and explain with radial H-like wave functions (ω f)

$$R_{n\ell}(r) = \frac{2Z_1^{3/2}}{n^{*2}} \left[\frac{(n-\ell-1)!(2+2a_b)_{n-\ell-1}}{\Gamma(2+2a_b)} \right]^{1/2} \left(\frac{2Z_1r}{n^*} \right)^{a_b} \times (5) \\ \times \sum_{j=0}^{n-\ell-1} \frac{(-2Z_1r/n^*)^j}{(n-\ell-1-j)!(2+2a_b)_j j!}$$

indexed with the explained below parameter (see Appendix) [20] a_b dependent on Z, n and ℓ . So, the effective quantum number $n^*=n-\ell+a_b$, allows to explain excited bound state energies within the H-like expression

$$E_{n\ell} = -\frac{Z_1^2}{n^{*2}}$$

Given partial correlation contributing to $g_L(r)$ may now be given an explicit dimensionless expression,

$$g_{L\ell \le 2}(x) = 2\sqrt{2\pi}\xi^{3} \sum_{n=n\ell}^{\infty} (2\ell+1)(2\xi x)^{2a_{b}} \times \frac{\Gamma(n+2a_{b}-\ell+1)(n-\ell-1)!}{n^{*4+2a_{b}}} \times \exp\left(\frac{\xi^{2}}{2n^{*2}}-\frac{2\xi x}{n^{*}}\right)^{*}$$
(6)
$$*\left[\sum_{j=0}^{n-\ell-1} \frac{(-2\xi x/n^{*})^{j}}{(n-\ell-1-j)!\Gamma(2+2a_{b}+j)j!}\right]^{2}$$

where $n_\ell\!=\!2$ for $\ell=0,\,1\,$ and $\,n_\ell\!=\!3$ for $\ell=\!2$.

Terms pertaining to excited states with $\ell \ge 3$ are taken hydrogenic [25] and explained with $a_b=0$ through H-like $R_{n\ell}(r)$ for Z_1 .

2.2. Diffusion state contributions

As far as two-body e-Z₁ continuous states are considered we consistently restrict the $\ell \ge 3$ to pure Coulomb ones with charge Z₁ (a_c=0 in the sequel). For relative angular momenta $\ell \le 2$, and positive relative energy e-Z₁. For relative angular momenta $\ell \le 2$, and positive we now have to consider [24]

$$R_{k\ell}(r) = \sqrt{\frac{2k}{r}} \frac{\prod_{s=1}^{\ell} \left(1 + s^2 / \eta^2\right)^{1/2}}{\left(1 - \exp\left(-2\pi\eta\right)\right)^{1/2}} \eta^{a_c - \ell} \left(\frac{\Gamma\left(1 + a_c - i\eta\right)}{\Gamma\left(1 + \ell\right) - i\eta} \left(x \sum_{p=0}^{\infty} \left(-1\right)^p \left(\frac{k^2 r}{2Z_1}\right)^p \left\{A_{2p} J_{1+2a_c + 2p}\left(\rho\right) - \frac{\rho}{2} B_{2p+1} J_{2+2a_c + 2p}\left(\rho\right)\right\}$$
(7)

where $\eta = Z_1/k$, while a_c relying on Z, ρ and k features the other positive energy and crucial QDM parameter (See Appendix).

Coefficients A_{2p} and B_{2p+1} are detailed as

$$A_0 = 1, A_2 = 1 + a_c, A_4 = (1 + a_c)(2 + a_c)/2$$
 (8)

$$B_1 = 0, B_3 = 1/3, B_5 = (8+5a_c)/15,$$

 $p \ge 3$:

$$p(2p-3)A_{2p} = [(p-1)(2p-3+2a_c)+(2p-3) (p+a_c)]A_{2p-2}-(2p-3+2a_c) (p-1+a_c)A_{2p-4}-2h^2A_{2p-6}$$

$$(p-1)(2p+1)B_{2p+1} = [(p-1)(2p+1+2a_c) + (2p-1)(p-1+a_c)]B_{2p-1} - (2p-1+2a_c)$$
$$(p-1+a_c)B_{2p-3} - 2h^2B_{2p-5}$$

The resulting partial-correlation function

$$g_{D\ell}(r) = \frac{1}{4\pi} \left(\frac{2\pi\beta\hbar^2}{m}\right)^{3/2} (2\ell+1) \times$$

$$\times \left(\sum_{0}^{\infty} \exp\left(\frac{-\beta\hbar^2k^2}{2m}\right) \{R_{k\ell}(r)\}^2 dk \right)$$
(9)

then appears through $y = \xi k / Z_1$ under the form

$$g_{D\ell \leq 2}(x) = \frac{\sqrt{2\pi}}{x} (2\ell+1) {\binom{\infty}{0}} dy \exp\left(\frac{-y^2}{2}\right) C(y,\xi) \times \left[\sum_{p=0}^{\infty} (-1)^p \left(\frac{y^2 x}{2\xi}\right)^p \left\{A_{2p} J_{\nu}(\rho) - \frac{\rho}{2} B_{2p+1} J_{\nu+1}(\rho)\right\}\right]^2$$
(10)

where $v = 1 + 2a_c + 2p$ with $\rho = 2\sqrt{2\xi x}$ and

$$C(y,\boldsymbol{\xi}) = y \frac{\prod_{s=1}^{\ell} (1 + s^2 y^2 / \boldsymbol{\xi}^2)}{1 - \exp(-2\pi\boldsymbol{\xi} / y)} \left(\frac{y}{\boldsymbol{\xi}}\right)^{2(a_c - \ell)} \times \left(\frac{\Gamma(1 + a_c - i\boldsymbol{\xi} / y)}{\Gamma(1 + \ell - i\boldsymbol{\xi} / y)}\right)^{2(a_c - \ell)}$$

At this level of presentation, it should be appreciated that the displayed QDM formalism entirely relies on the two parameters a_b and a_c . So, it is now timely to recall that a_b is derived from the very accurate (n, ℓ) ionization energies [20] while a_c is directly related to the departure from the Coulomb phase, which we denote $\delta_1(k^2)$ by [18]

$$\delta_{1}(k^{2}) = \arg \Gamma \left(1 + a_{c} - iZ_{1} / k \right) - \arg \Gamma \left(1 + \ell - iZ_{1} / k \right) + \frac{1}{2} \pi \left(\ell - a_{c} \right)$$
(11)

also a very well documented quantity. Our former assertion about the $a_b=a_c=0$ approximation for the

 $\ell \ge 3$ excited levels stems from detailed investigations of the Z=2 polarization model [25].

2.3 Spin effects

In hydrogenic systems, electron spin plays only a minim role essentially limited to relativistic calculations of the fine structure constant, pertaining relativistic modifications remaining small relative to the Bohr and non relativistic binding energy. The situation looks different in the He-sequence, because the total spin S=0 or 1 has to be included in the evaluations of $E_{n\ell}$ and $\delta_{\ell}(k^2)$. Energies of singlet and triplet states thus differ at most by 20 percent for the first excited states. As for as the present QDM framework is considered, this S-dependence is included within $a_b(n, \ell, Z, S)$ and $a_c(n, \ell, Z, S)$ with $\ell \leq 2$. (Practically, it suffices to include that Sdependence for low lying $\ell \leq 2$ levels). To determine those S-dependent states, were are thus led to envision a model with an electron orbiting in a field of a non-point-like ion, so the given wave functions do not exhibit the usual an antisymmetric form, and are distinct according to S = 0 or 1. Spin effects are then accounted through

$$g_{\ell \le 2}^{\overline{S}}(x) = \frac{3}{4} g_{\ell \le 2}^{S=1}(x) + \frac{1}{4} g_{\ell \le 2}^{S=0}(x), \quad (12)$$

leading to the more accurate expression

$$g(x) = g_F(x) + \sum_{\ell=0}^{2} g_{\ell}^{\overline{S}}(x) + \sum_{\ell>3} g_{\ell}(x)$$
(13)

for the total $e-Z_1$ correlation function.

These spin effects decay with increasing Z_1 . They are mostly significant for Z=2, with significant S=0, 1 discrepancies. Fig. 1a display ℓ =0,1 correlation functions with S = 0,1 for Z=2. The S discrepancy shows up as significant. Fig. 1b also displays same $g_{\Box}(x)$ contrasted to those of Z=4 (boron). Considered temperatures feature same parameter for both elements. So, one witnesses that this S-effect decreases when Z increases, whenever the same ionization is maintained.

2.4 Structure Effects

Our presently used QDM techniques imply that the pair $e-Z_1$ correlation function be computed through hydrogen-like wave functions with net charge $Z_1=Z-1$. The structure effects featured by the He-sequence are expressed with non integer a_b and a_c parameters. The latter highlight the discrepancy between He-like g(x) and H-like ones with equivalent point like charge. Figs. 2 exhibit partial

 $g_{\ell}(x)$ with $\ell=0,1$ or 2 for He, then contrasted to their H-like homologues.



Figure 1 – Partial correlation function gℓ(x) in terms of scattering states ℓ=0.1 for total spin s=0.1:
a) He 3-body plasma; b) He 3 body plasma contrasted to He-like B plasma



Figure 2 – Partial correlation functions out of bound states for H and He plasmas at T=4x10⁴ °K: a) ℓ =0.1 for H and He; b) ℓ =1 for H and He and ℓ =2 for He

3 Effective interaction e – Z1

3.1 General trends

Elaborating upon the above detailed evaluation of the total $e-Z_1$ correlation function of

$$g(r) = g_F(r) + g_{D\ell \le 2}(r) +$$

$$+ g_{L\ell \ge 3}(r) + g_{D\ell \le 2}(r) + g_{D\ell \ge 3}(r)$$
(14)

were are now entitled to proceed to the extraction of the T-dependent $e-Z_1$ effective interaction from Eq. (1). A first and instructive study concerns the

comparison of H-like $g^{(H)}(x)$ and He-like $g^{(He)}(x)$, with $x = r/\lambda$

To implement this matching it is appropriate to take the $e-Z_1$ effective interaction under the form

$$-\frac{\boldsymbol{\xi}}{\left(\boldsymbol{Z}-\boldsymbol{1}\right)^2}u(\boldsymbol{x}) = \frac{1}{\boldsymbol{\xi}}\ln\left[g\left(\boldsymbol{x}\right)\right]$$
(15)

depicted on Fig. 3 for ξ =2 and the He-like sequence $2 \leq Z \leq 26$. He-like u(x) gets closer to its H-like point-like limit when Z increases. Moreover, $g^{(He)}(x)$ values are directly contrasted to $g^{(H)}(x)$ values on Figure 4,



Figure 3 – $-\frac{\xi}{(Z-1)^2}u(x) = \frac{1}{\xi}\ln[g(x)]$ for $\xi=2$ and He-like plasmas with $2 \le Z \le 26$

through

$$-\frac{\xi}{(Z-1)^2}u^{He}(x) + \frac{\xi}{(Z-1)^2}u^{H}(x) = \frac{1}{\xi}\ln\left[g^{He}(x)/g^{H}(x)\right]$$
(15)

when ξ is fixed, a given T value is ascribed to a given Z value. One thus compares correlation

functions at different Z values and equivalent ionization stage.



Figure 4 – He-H discrepancies
$$-\frac{\boldsymbol{\xi}}{(Z-1)^2}u^{He}(x) + \frac{\boldsymbol{\xi}}{(Z-1)^2}u^{H}(x) = \frac{1}{\boldsymbol{\xi}}\ln\left[g^{He}(x)/g^{H}(x)\right]$$

3.2 Analytic expressions

In order to secure a transparent and instructive comparison with standard effective interactions currently used in hydrogenic plasmas, we try to put the present He-like pseudopotential under a form as close as possible to the finite T extension of the Kelbg-Deutsch potential [2,4-6] as proposed by Gombert and Wagenknecht et al. [7]. Toward this goal, we thus recall the Kelbg expression $(\xi_{\rm H} = Z\beta^{1/2})$ [2]

$$-\frac{\xi_{H}}{Z^{2}}U_{K}(x) = \frac{1}{x} \Big[1 - \exp(-2x^{2}) \Big] + \sqrt{2\pi} \Big[1 - Erf(\sqrt{2}x) \Big]$$
(16)

in terms of the Error function

$$Erf(x) = \frac{2}{\sqrt{\pi}} {\binom{x}{0}} \exp(-t^2) dt =$$

$$= \frac{2}{\sqrt{\pi}} \sum_{n=0}^{\infty} \frac{(-1)^n x^{2n+1}}{n! (2n+1)}$$
(17)

yielding $-\frac{\xi_{H}}{Z^{2}}Uk(0) = \sqrt{2\pi}$ and a Z-independent slope at the origin without x² term in the small x expansion. A very closed related expression to $U_K(x)$ features the simpler Deutsch expression [4-6]

$$-\frac{\xi_{\rm H}}{Z^2} U_{\rm D}(x) = \frac{1}{x} \left(1 - e^{-\sqrt{2\pi}x} \right)$$
(18)

Both $U_K(x)$ and $U_D(x)$ are mostly accurate in hydrogenic plasmas at very high (if not infinite) temperature. To remedy for this drawback Gombert and Wagenknecht et al [7] came up with the finite T-extension

$$-\frac{\boldsymbol{\xi}_{H}}{Z^{2}}U_{GW}(x) = \frac{1}{x} \left[1 - \exp(-2x^{2}) \right] + A_{H} \left[1 - Erf\left(\frac{2\sqrt{\boldsymbol{\pi}}}{A_{H}}x\right) \right]$$
(19)

where

$$A_{H} = (2\pi)^{\frac{1}{2}} + \pi \left(\frac{\pi}{3} - 1\right) \boldsymbol{\xi} + \\ + 2(2\pi)^{\frac{1}{2}} \left(-\frac{\pi^{2}}{6} + \frac{\pi}{3} + \frac{\boldsymbol{\xi}(3)}{2}\right) \boldsymbol{\xi}^{2} + O(\boldsymbol{\xi}^{3})$$
(20)

with the small x-expansion

$$-\frac{\xi}{Z^2}U_{GW}(x) = A_H + 2x - 2\left(1 - \frac{8\pi}{3A_H^2}\right)x^3 + \dots (21)$$
Now, we turn toward the He-like effective interactions fulfilling

$$(\xi_{\text{He}} = (Z-1)\beta^{1/2} = \xi_{\text{H}} / (\alpha + 1) \text{ where } \alpha = 1/(Z-1))$$

$$-\frac{\xi_{He}}{(Z-1)^{2}}U_{He}(x) = -\frac{(\alpha+1)^{2}\xi_{He}}{Z^{2}}U_{He}(x) =$$

$$= \frac{1}{\xi_{HE}}\ln[g^{(He)}(x)]$$
(22)

and valid at any temperature T, because bound and scattered states are explicitly included through the QDM approach. The given He-like effective interaction $U_{\text{He}}(x)$ is supposed to yield back $U_{\text{GW}}(x)$ for $\alpha = 1/(Z-1) \rightarrow 0$.

First, $U_{GW}(x)$ gets validated for any finite temperature T with a A_H parametrization for, $\xi \sim 1$ coincident with above expression (19) for $\xi <<1$. Then, we reach a hydrogenic pseudopotential valid at any T. Next, we introduce an α -parametrization acknowledging the He-like sequence (mostly Z=2 \rightarrow 26). Then, we arrive at the α -dependent expression

$$\frac{(\boldsymbol{\alpha}+1)^{2}\boldsymbol{\xi}}{Z^{2}}U_{He}(x) = \frac{1}{x} \Big[1 - \exp\left(-2x^{2} - \boldsymbol{\alpha}x^{3}\right) \Big] + \tag{23}$$
$$+A_{He} \Big[1 - Erf(B_{He}x) \Big]$$
$$A_{Z} = A_{He} = A(\boldsymbol{\xi}, \boldsymbol{\alpha}) = A(\boldsymbol{\xi}, \boldsymbol{\alpha} = 0)f(\boldsymbol{\alpha})$$
$$A(\boldsymbol{\xi}, \boldsymbol{\alpha} = 0) = \sqrt{2\pi} + \boldsymbol{\xi}\frac{a_{0} + a_{1}\boldsymbol{\xi} + a_{2}\boldsymbol{\xi}^{2}}{1 + a_{3}\boldsymbol{\xi} + a_{4}\boldsymbol{\xi}^{2}} \tag{23a}$$
$$f(\boldsymbol{\alpha}) = 1 + \boldsymbol{\alpha} Erf\left[b\boldsymbol{\alpha}\right], \quad f(\boldsymbol{\alpha} = 0) = 1$$
$$B_{He} = B\left(\boldsymbol{\xi}, \boldsymbol{\alpha}\right) = \frac{B\left(\boldsymbol{\xi}, \boldsymbol{\alpha} = 0\right)}{g\left(\boldsymbol{\xi}, \boldsymbol{\alpha}\right)}$$
$$B\left(\boldsymbol{\xi}, \boldsymbol{\alpha} = 0\right) = \frac{2\sqrt{\pi}}{A\left(\boldsymbol{\xi}, \boldsymbol{\alpha} = 0\right)} \tag{23b}$$

and

$$g(\boldsymbol{\xi}, \boldsymbol{\alpha}) = 1 + \boldsymbol{\xi}^{2} (b_{0} + b_{1} \boldsymbol{\xi}^{2}) Erf [b_{2} \sqrt{\boldsymbol{\alpha}}]$$
$$g(\boldsymbol{\xi}, \boldsymbol{\alpha} = 0) = g(\boldsymbol{\xi} = 0, \boldsymbol{\alpha}) = 1$$

Coefficients a_0 , a_4 , a,b,b_0,b_1 et b_2 are given on Table 2.

 Table 2 – Coefficients involved in Eqs. (23 a-b)

$a_0 = .14827548$	$a_1 = .0155383$	$a_2 = .00421951$
$a_3 = .00027919$	$a_4 = .0116586$	
a = 1.75972	b = .291829	
$b_0 = .852678$	$b_1 = .0425476$	$b_2 = .00920166$

Figure 5 feature A and B- ξ variations in terms of α parameter. Curves with $\alpha = 0$ pertain to U_{GW}(x) interaction valid for any T value. Kelbg's parameters get retrieed for A_k = $\sqrt{2\pi}$ and B_k= $\sqrt{2}$ at $\alpha = \xi = 0$. A is obviously more α -sensitive than

B. Permuting α and ξ roles, we get the ξ parametrized A and B in terms of α , on Figure 6. We do not pay much attention to $\xi > 4$, A and B values, featuring lower temperatures when H-like and He-like ions become scarce.



Figure 5 – A and B (Eqs.23 a,b) for He-like effective interactions in terms of ξ and $0 \le \alpha \le 1$ respectively

 $U_{GW}(x)$ data are also retrieved for $\xi <<1$ and $\alpha = 0$, with a very good accuracy. Numerically speaking, the present $U_{He}(x)$ fits the e-Z₁ radial distribution function with a 1-2 percent precision. Near x = 0, it also fulfils

$$-\frac{(\boldsymbol{\alpha}+1)^{2} \boldsymbol{\xi}}{Z^{2}} U_{He}(x) \cong A + 2 \left(1 - \frac{A_{He}B_{He}}{\sqrt{\pi}}\right) x +$$
(24)
$$+\boldsymbol{\alpha} x^{2} - 2 \left(1 - \frac{A_{He}B_{He}^{3}}{3\sqrt{\pi}}\right) x^{3} + \dots$$



Figure 6 – A and B (Eq. (23a-b)) for $U_{He}(x)$ In terms of $0 \le \alpha \le 1$ and $2 \le \xi \le 3$

highlighting now an x^2 term, absent in previous H-like effective interactions. Moreover, the slope at x=0

$$P_{\rm He} = 2 \left(1 - 2 \frac{f(\alpha)}{g(\xi, \alpha)} \right) \equiv P_0(\xi, \alpha)$$
 (25)

where $P(\xi, \alpha = 0) = -2 = P_H$ appears α -and T-dependent.

3.3 Numerics [25]

Figures 7a-c feature the above displayed e- Z_1 effective interactions systematically confronted to their Hydrogen-like homologues for Z=2, 10 and 92, respectively. The e- Z_1 distance is scaled by the electron thermal wavelength $\hat{\lambda}$ in a dense plasma with $T_e = T_i$, where T_i designates the same ion temperature for ion Z and ion Z-1.

D denotes Deutsch expression (18), GW is for Gombert-Wagenknecht expression (19) and K is for Kelbg expression (16). The Helium-like effective interactions (23) are thus compared to their various Hydrogen-like counterparts $U_K(x)$ (Eq 16), $U_D(x)$ (Eq.18) and $U_{GW}(x)$ (Eq.19). The He-like –H-like discrepancies are strongly noticeable for $x \le 1$, and increase with Z. These results demonstrate clearly that WDM properties computed for He-like Be, for instance, cannot be approximated by the H-like effective interaction (16, 18, 19). In this connection, it is pretty instructive to test the low-T behavior of expression (23) with the dominant H-like approximation [27]

$$g_{eZ_1}(x) = Log \left[2\sqrt{\pi} \boldsymbol{\xi}^3 e^{\boldsymbol{\xi}^2/2 - 2\boldsymbol{\xi}x} \right] / \boldsymbol{\xi}$$
(26)

denoted as H_{bd} in Figures 8 which lies pretty close to $U_{GW}(x)$ for $x \le 0.5$, while $g_{eZ1}(0) \sim U_{GW}(0)$ is well represented by $Log(g_{ij}(0, \gamma))$ where $\gamma = 2\xi^2$ and

$$g_{ij}(0,\boldsymbol{\gamma}) = 1 + \sqrt{\pi \boldsymbol{\gamma}} + \sum_{n=0}^{\infty} \frac{\Gamma\left(1+\frac{n}{2}\right)}{n!} \boldsymbol{\zeta}(n+2) \boldsymbol{\gamma}^{\frac{n}{2}+1}$$

In terms of Gamma $\Gamma(x)$ and Zeta $\zeta(x)$ functions respectively. As T increase with no limits, the Helike behavior (23) tends to join the H-like homologues (16,18-19), with a marked saturation observed for T > J (Ryd) with [28]

$$J = Z_1^2 - \frac{5}{4}Z_1 + 0.315311 - 0.01707\frac{1}{Z_1} +$$

$$+ 0.00068\frac{1}{Z_1^2} + 0.00164\frac{1}{Z_1^3} + 0.00489\frac{1}{Z_1^4}$$
(27)

nonrelativistic ionization energy of ion Z₁.

Hbd refers to the H-like bound state contribution (26). D,GW and K attributions are the same as on Figures 7.

4 Ionization in dense 3-component plasmas

4.1. Notations

It is convenient to write the canonical ionization in a 3-component (e, ion Z, ion Z_1) plasma under the form

$$\boldsymbol{v} = \frac{\boldsymbol{\rho}_z}{\boldsymbol{\rho}_z + \boldsymbol{\rho}_{z_1}} = \frac{\boldsymbol{\rho}_z}{\boldsymbol{\rho}_I}$$
(28)

Quasi-neutrality then features $\rho_e = Z\rho_z + Z_1\rho_{Z1}$ with the Debye length $\lambda_D^{-2} = 4\pi\beta\rho_I Z(Z_1 + 2\nu)$ and

the diffraction parameter $(\overline{\lambda} = \frac{\hbar}{\sqrt{m_{k_{p}}T}})$

 $\boldsymbol{\eta} = \frac{\boldsymbol{\bar{\lambda}}}{\boldsymbol{\lambda}_{D}} \text{ fulfilling}$

$$\boldsymbol{\eta}^{2} = 4\pi\boldsymbol{\beta}\boldsymbol{\rho}_{I}\boldsymbol{\lambda}^{2}Z(\boldsymbol{Z}_{1}+2\boldsymbol{\nu})$$

Moreover, the total density $\rho = (Z + x)\rho I$ allows to explain the plasma parameter as $(\xi = Z\overline{\lambda})$ under the form

$$\Lambda = \frac{1}{4\pi\rho\lambda_D^3} = \frac{Z_1 + 2\nu}{Z + \nu}\eta\xi$$
(29)

Numerically, one thus gets

$$\boldsymbol{\eta} = 4.32310^{-7} \left[Z \left(Z_1 + 2\boldsymbol{\nu} \right) \right]^{1/2} \frac{\boldsymbol{\rho}_I^{1/2} \left(cm^{-3} \right)}{T^{3/2} \left({}^{\circ}\boldsymbol{K} \right)}$$
(30)

$$\mathbf{\Lambda} = 2.4210^{-4} \frac{\left[Z\left(Z_{1}+2\nu\right)\right]^{3/2}}{Z+\nu} \frac{\rho_{I}^{1/2}(cm^{-3})}{T^{3/2}\left(^{\circ}K\right)}$$



40





- (a) Z=2 for 4 < T(eV) < 4000
- (b) (b).Z=10 for 4 < T(eV) < 4000
- (c) Z=92 for 0.4 < T(keV) < 400



Figures 8 – He-like effective interaction (23) contrasted to its H-like homologues (16,18,19) $U = -\frac{g_{II}}{z^2} U_{GW,K,D}$ in a He plasma, with Z=4

4.2. Ionization equilibrium

At equilibrium in a 3-component plasma the canonical free energy F fulfills $\frac{dF}{dv} = 0$ for a given (T, ρ_I) pair. It then appears appropriate to split the given partial derivative as

$$\frac{dF_0}{d\boldsymbol{\nu}} + \frac{dF_{ex}}{d\boldsymbol{\nu}} + \frac{dF_c}{d\boldsymbol{\nu}} + \frac{dF_{\varrho}}{d\boldsymbol{\nu}} = 0$$
(31)

First, the ideal contribution is explained through

$$\frac{\boldsymbol{\beta}}{V} \frac{dF_0}{d\boldsymbol{\nu}} = \boldsymbol{\rho}_I \ln \left[\sqrt{\frac{\boldsymbol{\pi}}{2}} \frac{\boldsymbol{\eta}^3}{\boldsymbol{\Lambda}} \frac{\boldsymbol{\nu}(\boldsymbol{Z}_1 + \boldsymbol{\nu})}{(1 - \boldsymbol{\nu})(\boldsymbol{Z} + \boldsymbol{\nu})} \boldsymbol{\sigma}(\boldsymbol{T}) \right] \quad (32)$$

with

$$\boldsymbol{\sigma}(T) = \sum_{n=1}^{\infty} n^2 \left[\exp\left(\boldsymbol{\beta} I_{Z_1} Z^2 / n^2\right) - 1 - \frac{\boldsymbol{\beta} I_{Z_1} Z^2}{n^2} \right]$$
$$I_{Z_1} = \frac{Z_1}{\boldsymbol{\eta}^2}$$
(32a)

then, we have the Coulomb part $(\beta = 1/k_BT)$ and the exchange one

$$\frac{\boldsymbol{\beta}}{V}\frac{dF_c}{d\boldsymbol{\nu}} = -\boldsymbol{\rho}_I \boldsymbol{\Lambda} \frac{Z + \boldsymbol{\nu}}{Z_1 + 2\boldsymbol{\nu}}$$
(33)

$$\frac{\boldsymbol{\beta}}{V}\frac{dF_{ex}}{d\boldsymbol{\nu}} = \frac{\sqrt{\boldsymbol{\pi}}}{8}\boldsymbol{\rho}_{I}\frac{\boldsymbol{\eta}^{3}}{\boldsymbol{\Lambda}}\frac{Z_{1}+\boldsymbol{\nu}}{Z+\boldsymbol{\nu}}\left[1+\frac{\sqrt{\boldsymbol{\pi}}}{12\sqrt{3}}\frac{\boldsymbol{\eta}^{3}}{\boldsymbol{\Lambda}}\frac{Z_{1}+\boldsymbol{\nu}}{Z+\boldsymbol{\nu}}\right] \quad (34)$$

Quantum corrections $\frac{\partial F_o}{\partial v}$ are also split, so we get the first contribution under the form

$$\frac{\boldsymbol{\beta}}{V}\frac{dF_1}{d\boldsymbol{\nu}} = \boldsymbol{\rho}_I \frac{\boldsymbol{\eta}^2}{Z(Z_1 + 2\boldsymbol{\nu})} xI_1$$
(35)

with

In the above A_e , A_z and A_{z1} feature respectively the three T-dependent effective interactions [30]

$$u_{ee}(r) = -\frac{Z}{r} \left[1 - e^{-2r^2/\overline{\lambda}^2} \right] - \frac{ZA(\xi)}{\overline{\lambda}} \left[1 - erf(B(\xi)r/\overline{\lambda}) \right]$$

$$u_{e_{\tau}}(r) = -\frac{Z_{1}}{r} \left[1 - e^{-2r^{2}/\overline{\lambda}^{2} - \alpha r^{3}/\lambda^{-1}} \right] - , \quad (36)$$
$$-\frac{Z_{1}A(\boldsymbol{\xi}_{1}, \boldsymbol{\alpha})}{\overline{\lambda}} \left[1 - erf\left(B(\boldsymbol{\xi}_{1}, \boldsymbol{\alpha})r / \overline{\lambda}\right) \right]$$
$$u_{ee}(r) = \frac{1}{r} \left[1 - e^{-2r^{2}/\lambda_{ee}^{-2}} \right] + \frac{A(\boldsymbol{\xi}_{e})}{\overline{\lambda}_{ee}} \left[1 - erf\left(B(\boldsymbol{\xi}_{e})r / \overline{\lambda}_{ee}\right) \right]$$

with $A_e \equiv A(\boldsymbol{\xi}_e), A_z \equiv A(\boldsymbol{\xi}) \text{ and } A_{z_1} = A(\boldsymbol{\xi}_1, \boldsymbol{\alpha})$

where
$$\boldsymbol{\xi} = Z \overline{\boldsymbol{\lambda}}, \boldsymbol{\xi}_1 = Z_1 \overline{\boldsymbol{\lambda}}$$
 and $\boldsymbol{\xi}_e = \overline{\boldsymbol{\lambda}}_{ee} = \sqrt{2} \overline{\boldsymbol{\lambda}}$

Their, putting the Fourier transform of $U_{ee}(r)$ under the form $(y = k\lambda)$

$$u_{ee}(y) = 4\pi \overline{\lambda}^{2} \left(\frac{1}{y^{2}} - \frac{1}{2} S_{e}(y, \xi_{e}) \right), \qquad (37)$$

while explaining the determinant of the above three U_{ij} 'S interactions in k-space, as

 $\sqrt{\frac{\pi}{2}} \frac{\eta^3}{\Lambda} \frac{\nu(Z_1 + \nu)}{(1 - \nu)(Z + \nu)} \sigma(T) =$

 $= \exp \left[f_{c} + f_{ex} + f_{Q1} + f_{Q2} \right]$

$$D(k) = 1 + \beta \rho_{I} \left\{ (Z_{1} + \nu) u_{ee}(k) + [Z^{2}(x) + Z_{1}^{2}(1 - \nu)] \frac{4\pi}{k^{2}} \right\} +$$

$$+ \beta^{2} \rho_{I}^{2} (Z_{1} + \nu) \left\{ [Z^{2}x + Z_{1}^{2}(1 - \nu)] u_{ee}(k) \frac{4\pi}{k^{2}} - (1 - \nu) [u_{ee_{I}(k)}]^{2} - \nu [u_{ee(k)}]^{2} \right\}$$
(38)

$$-\boldsymbol{\beta}^{3}\boldsymbol{\rho}_{1}^{3}\boldsymbol{\nu}(1-\boldsymbol{\nu})(Z_{1}+\boldsymbol{\nu})\left[Zu_{e_{z_{1}}}(k)-Z_{1}u_{e_{z}}(k)\right]^{2}\frac{4\boldsymbol{\pi}}{k^{2}}$$

with Coulomb ion-ion interactions

$$u_{zz}(k) = Z^{2}u_{pp}(k), \ u_{z_{1}z_{1}}(k) = Z^{2}_{1}u_{pp}(k),$$

$$u_{zz_{1}}(k) = ZZ_{1}u_{pp}(k)$$
(39)

where [29, 30]

$$f_c = \Lambda \frac{Z + \nu}{Z_1 + 2\nu} \tag{41a}$$

(41)

$$f_{ex} = \frac{\sqrt{\pi}}{8} \frac{\eta^3}{\Lambda} \frac{Z_1 + \nu}{Z + \nu} \left[1 + \frac{\sqrt{\pi}}{12\sqrt{3}} \frac{\eta^3}{\Lambda} \frac{Z_1 + \nu}{Z + \nu} \right]$$
(41b)

and

$$f_{\varrho_1} = -\frac{\eta^3}{Z(Z_1 + 2\nu)} I_1 \qquad (41c)$$

$$f_{Q2} = -\frac{\Lambda}{\eta} \frac{1}{\pi} \frac{Z + \nu}{Z(Z_1 + 2\nu)} I_2 \qquad (41d)$$

4.3. Numerical results

Conspicuous dependences of v on $\rho_1 = \rho_z + \rho_{z1}$ are detailed on Figs. 9 a-b, for He(Z=2) and C(Z=6) plasmas. The left and decaying portion which is mostly T-dependent of v versus ρ_1 shows a rather weak α -dependence, especially for Carbon, while

and $u_{pp}(k) = \frac{4\pi}{k^2}$,

allows us to explicit the 2nd quantum contribution as

$$\frac{\boldsymbol{\beta}}{V}\frac{dF_2}{d\boldsymbol{\nu}} = \boldsymbol{\rho}_I \frac{\boldsymbol{\Lambda}}{\boldsymbol{\eta}} \frac{1}{\boldsymbol{\pi}} \frac{Z + \boldsymbol{\nu}}{Z(Z_1 + 2\boldsymbol{\nu})} x I_2, \qquad (40)$$

with $(y = k \mathbf{\lambda})$

$$I_{2} = \begin{pmatrix} \overset{\bullet}{}_{0} y^{2} dy \left[\frac{dD(y) / dx}{D(y)} - \frac{2Z}{y^{2} + \eta^{2}} + \frac{1}{2} S_{e}(k, \boldsymbol{\xi}_{e}) \right]$$
(40a)

Finally, the above dF/dv=0 relation boils down to

the increasing density-dependent portion appears strongly α -resolved. This second behavior documents the fact that in a very dense plasma medium the nonpointlike structure of ion Z_1 is quantitatively perceived.

Moreover, for both Z = 2 and 6, $\alpha \neq 0$ produces the smallest ionization, while the bare Coulomb interaction yields the highest. The ionization patterns featured on Figs. 9 show clearly that even a finite-T effective e-Z and hydrogenic interaction would not be able to reproduce them. These outputs demand the implementation of an accurate albeit analytic effective quantum defect approach as evidence by Eqs. (6,10).



Figure 9 – Ionization $v = \rho_z/\rho_1$ in a 3 body e-Z-Z₁ plasma with partial sums involved in Eq.(41) in terms of $\rho_1 = \rho_z + \rho_{z_1}$. a) He at T = 2.021x10⁵ °K for a = 0 and 1; b) C at T = 1.819x10⁶°K for a = 0 and 2

5 Conclusions

To summarize, we have demonstrated genuine and He-like effective interactions in dense and hot plasmas analytically derived through explicit wave functions. The novel pseudopotentials have been contrasted to their various H-like counterparts ($\alpha =$ 0), and thus display highly significant improvements upon the latter. Both approaches converge with increasing atomic number and plasma temperature. Their respective impact on the ionization parameter is also significantly documented, mostly at high density in the pressure dominated regime, which lead us to expect much more accurate results for the equation of state, Hugoniots and transport properties of warm dense matter plasmas of present concern, especially when alpha is larger than one (see Figs. 9). An obvious test of choice for these novel He-like effective interaction could thus be the determination of bremsstrahlung coefficients extending former Hlike ones obtained through expression (18) [31].

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Appendix a_b and a_c in the Quantum defect method (QDM)[32]

According to Simons [22], it appears convenient to start from the Fues-like expression for the nonrelativistic hamiltonian for the optical electronhydrogenic core. The hydrogenic core is kept in the 1s ground state. The given hamiltonian thus reads as $(\hbar = m = e = 1)$

$$H = -\frac{\nabla}{2} - \frac{Z_1}{r} + \sum_{\ell=0}^{\infty} P_{\ell} \frac{B(\ell)}{v^2}$$
(A.1)

with projection operator $P_{\ell} = \sum_{m=-\ell}^{m+\ell} (\ell m) (\ell m)$ over

subspace pertaining to angular momentum ℓ , while B_{ℓ} is an adjustable parameter through experimental or theoretical inputs. Pertaining radial equations thus appear under hydrogen like form. Addressing first the bound states set, one has

$$\left[-\frac{1}{2}d^{2}/dr^{2}+a_{b}(a_{b}+1)/2r^{2}-Z_{1}/r\right]\mu(r)=E\mu(r) (A.2)$$

has the solutions

$$E = -Z_1^2 / 2(n-1+a_b)^2$$
 (A.3)

$$\boldsymbol{\mu}(\boldsymbol{r}) = Cr^{a_{b}+1} \exp(-\boldsymbol{\varepsilon}\boldsymbol{r}) L^{2a+1}_{N-l-1}(\boldsymbol{\varepsilon}\boldsymbol{r}) \qquad (A.4)$$

with
$$a_b = -\frac{1}{2} + \frac{1}{2} \Big[(2l+1)^2 + 8B_b \Big]^{1/2}$$

 $\varepsilon = Z / (n-1+a_b)$ (A.5)

and where L_p^q is a generalised Laguerre polynomial. C denotes a normalisation constant while $\mu(r)$ is quadratically integrable provided

$$a_1 > -\frac{3}{2} \tag{A.6a}$$

et
$$n - l > 1$$
 (A.6b)

We briefly recall the most significant properties,

(1) The solution of the radial equation (A.2) is analytical.

(2) For a given l series, one single parameter $(a_b or B_b)$ determines an orthonormal set of eigen functions and the corresponding spectrum.

(3) The choice of a_b is related to the definition of a quantum defect for a series, as can be seen from equation (A.3)

(4) The Fues model appears as a generalisation of the hydrogen case, with the introduction of an effective 'non-integer l'.

With increasing v, the energies and eigen functions behave 'asymptotically' like those of hydrogen. This extension of the polarization model $\ell \geq 2$ [24] toward larger values yield wave functions without antisymmetrization albeit distinct for total spin S=0 or 1. It is also worthwhile mentioning that B_b may be given the rather accurate approximant [22]

$$B_{b} \approx -\frac{1}{2} \alpha e^{2} \frac{\left\langle r^{-4} \right\rangle_{H}}{\left\langle r^{-2} \right\rangle_{H}}$$
(A.7)

in terms of the Z₁ core polarizability in 10^{-24} cm² and hydrogenic radial averages $\langle r^{-p} \rangle_{H}$ with p integer >0. Similarly, corresponding positive energy continuum states show up as eigenstates of Eq. (A.1) with a B_c parameter featuring a_c through $\ell(\ell+1)+2B_{c} = a_{c}(a_{c}+1)$ a_b and a_c are related by the Levinson theorem near the ionization edge with

$$a_b(n \to \infty, \ell) = a_c(k = 0, \ell)$$
 (A.8) Z

Present QDM phase shifts w.r.t. Coulombic ones, are then givent as $(\eta = Z_1/k)$ [21]

$$\delta_{\ell}(k^{2}) = \arg \Gamma(1 + a_{c} - i\eta) -$$
(A.9)
$$-\arg \Gamma(1 + \ell - i\eta) + \frac{\pi}{2}(\ell - a_{c})$$

in terms of a_c . $\delta_\ell(k^2)$ and a_c are both dependent on Z and S.

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Preparation method of tungsten oxide and metallic tungsten nano-powders using degreased cotton

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A simple method for producing nanopowders of tungsten oxides and metallic tungsten using degreased cotton is proposed. Ammonium tungstate $NH_4W_{12}O_{40}$ was used as a precursor. A medical cotton wool was chosen for experiment. Structural characterizations of nanopowders were performed using X-ray diffraction (XRD) and Raman spectroscopy. Raman Spectra was obtained by NTegra Spectra (NT-MDT), where the light source is blue laser ~473 nm. Analyses of XRD spectra showed that nanopowders have a monoclinic structure. The morphology of synthesized nanopowders was studied using scanning electron microscopy (SEM). The size of nanocrystals was estimated with Scherrer's formula. The effect of annealing temperature on nanoparticle sizes was investigated. The Raman spectra of the obtained samples were studied as a function of the synthesis temperature. In the Raman spectra, broading and red shift of the Raman bands with decreasing size are observed. The most pronounced Raman peaks are assigned to the characteristic vibrations according to the available structural data.

Key words: nanopowders, nanoparticles, tungsten oxide, tungsten. PACS number (s): 61.10.Nz; 61.46.+w; 63.20.-e; 81.05.Hd; 81.20.-n.

1 Introduction

Tungsten and its oxides have found wide practical application. Recently, nanoscale materials based on tungsten oxides have particular interest due to their electronic properties. Tungsten oxide is an n-type semiconductor and has excess free electrons; therefore, it has found application as electrochromic [1], photochromic material [2], photocatalyst [3] and gas sensors [4]. Metal oxide/hydroxide composites such as MnO₂, WO₃, NiO, and noble metals (Ag, Au, Pt) are perspective materials as electrode for supercapacitors [5], since they can improve the specific capacitance, conductivity, chemical and thermal stability of electrode materials. Electrodes based on WO₃*2H₂O show significant power and energy efficiency at high charge/discharge rates [6], energy storage is almost 100%. This makes it possible to use electrodes with a large mass and high volumetric capacity.

There are various methods for producing tungsten oxide nanoparticles, such as sonochemical

synthesis [7], precipitation from acid [8], thermal decomposition [9], ion exchange [10], template directed synthesis [11-12] and hydrothermal reactions [13-14]. In this paper, a method for formation of metal and oxide tungsten nanopowders using a fibrous matrix in the form of defatted cotton is proposed. This novel and facile method with the use of degreased cotton was recently applied for the synthesis of cobalt oxide nanoparticles [15].

2 Materials and methods

An degreased cotton (0.5 g) was impregnated with aqueous solution of ammonium metatungstate $(NH_4)_6H_{12}W_{12}O_{40}*H_2O$ (0.01M). The solution with cotton was processed in an ultrasonic bath for 30 minutes to achieve a homogenous substance. Then impregnated with precursor degreased cotton was collected and squeezed. After that the cotton was dried in a vacuum and annealed for 1 hour in air in the tube furnace with a heating rate 1°C/min. The annealing temperature was varied from 400 to 700°C. It is possible to carry out reductive chemical reactions using of hydrogen atmosphere during annealing and to obtain nanopowders of tungsten metal.

The crystal structure of the sample was studied by X-ray diffraction (MiniFlex Rigaku) with Cu K α radiation. The Raman spectra were taken using an NTegra Spectra (NT-MDT) spectrometer. A blue laser with a wavelength of 473 nm was used as the excitation source. The irradiation time of the samples by laser radiation was 30 s and the spot diameter on the sample was 2 µm. At 100% intensity, the laser power was 35 mW. Scanning electron microscopy (SEM) images were performed on a Quanta3D200i (FEI) scanning electron microscope.

3 Results and discussion

Figure 1 shows the XRD patterns of the WO₃ synthesized at temperatures from 400 to 700° C (a) and metallic tungsten obtained by reduction of WO₃ in hydrogen atmosphere at temperatures 550 to 850°C (b). All peaks have a good agreement with the standard monoclinic WO₃ spectrum. Moreover,

there are no impurity peaks found in the XRD patterns. The obtained results indicate that the wellcrystallized WO₃ and metallic W samples of high purity are produced. According to Scherrer's formula, $D = 0.89\lambda/(B\cos\theta)$ (where D is the mean size of crystallites; λ is the X-ray wavelength; θ is the Bragg angle; and B is the line diffraction broadening of a peak at half the maximum intensity, which is calculated using obtained XRD pattern), the crystalline size of WO₃ is estimated to be 7 nm in case of annealing temperature 400°C and about 300 nm for 800°C.

It is known that the smaller crystallite sizes, the broader X-ray peaks. Thus, analyzing XRD data of obtained samples it can be concluded that the sizes of tungsten and tungsten oxide crystals increase with synthesis temperature. However, the formation of the WO₃ crystal phase is limited by the temperature of the synthesis reaction, so low-temperature synthesis requires a much longer time. As the annealing temperature is increased, the XRD lines become narrow, hence, this indicates that the crystallite size in the WO₃ powder increases.



Figure 1 – XRD spectra: a) WO₃ obtained at temperatures from 400 to 700°C, b) W powder reduced at temperatures from 550 to 850°C in hydrogen atmosphere

The SEM morphology of the synthesized WO₃ powders has a good agreement with the X-ray data. It is seen from Fig. 2 that the crystallite sizes of the obtained WO₃ samples grow with the synthesis temperature. This is due to the fact that individual nanoparticles begin to interact and form larger crystals with increasing temperature.

Raman spectra of the samples obtained at different temperature conditions were studied.

The main vibrational modes for the WO₃ lattice are valence vibrations with a change of bond lengths (v), deformation vibrations with change of the angles between the bonds – planar (δ) and extra-plane (γ). It is known that these modes of tungsten oxide are in the frequency values ~807, ~716, ~271 cm⁻¹, which correspond to the stretching of the O-W-O, W-O bonds and O-W-O bending (see Table 1).



Figure 2 – SEM image of WO₃: a) after annealing at 400°C and b) 800°C, c) metallic W powders obtained from WO₃ reducing at temperature 400°C and d) 800°C

Vibrational mode	WO ₃ (400 ⁰ C)	WO ₃ (800 ⁰ C)	literature
V (O-W-O)	798	804	808
V (W-O)	683	715	717
Vibrations of groups WO ₂ W	-	-	436
δ (Ο-W-Ο)	-	372	376
δ (Ο-W-Ο)	321	326	328
δ (Ο-W-Ο)	251	272	273
W-W			221
Lattice mode	-	-	187
Lattice mode	108	133	136

Table 1 – Unaracteristic Raman frequencies (cm ⁻¹) of the WO_3 and filterature of	ire data
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Raman spectra of WO₃ at different annealing temperature are shown in Figure 3. It is seen from the figure, the main peak around ~ 800 cm⁻¹ shifts and narrows, depending on the annealing temperature. It is obvious from Table 1 that the position of the Raman lines for WO₃ samples synthesized at 400°C and 800°C are slightly different. It is known that the position of the Raman lines depends on the size of the crystallites, for example, in work [16] it is shown that as the crystallite size increases, the position of the Raman lines shifts toward higher frequencies. This is due to the fact that as the size of the nanocrystals decreases, the surface begins to play an increasingly important role, since the lattice constant and the melting point decrease. These theoretical and experimental data make it possible to explain the dependence of Raman scattering on the size of tungsten oxide nanoparticles. The broadening of the Raman peaks at ~805 cm⁻¹, ~ 716 cm⁻¹ and ~ 271 cm⁻¹ indicates a changing in the vibrational modes of WO₃ nanoparticles obtained at low annealing temperatures, and a decrease in the frequency of Raman vibrational modes indicates a softening of the phonon spectrum in nanoparticles WO₃.



Figure 3 – Raman spectra of the obtained tungsten oxides as a function of the annealing temperature

Figure 4.a shows the dependence of the half-width of the basic mode E_g as a function of the annealing

temperature. With increasing temperature, the halfwidth of the peaks decreases. The broadening of the Raman peaks at \sim 805 cm-1, \sim 716 cm-1, and \sim 271 cm-1 can be attributed to the broadening of the Raman vibrational modes in WO3 nanoparticles obtained at

low annealing temperatures. It is also seen that the main peak around \sim 715 cm-1 shifts towards low frequencies (Figure 4b).



Figure 4 – The dependence of the half-width of the E_g mode about ~ 805 cm⁻¹ as a function of the annealing temperature (a) and the dependence of the line position about ~ 715 cm⁻¹ on the annealing temperature (b)

It is known that with decreasing particle sizes to nanometer scales, optical Raman modes shift toward lower wave numbers [17]. The main causes of the Raman redshift of semiconductors can be caused by the size of the crystallites, the temperature (thermal induced expansion and attenuation of bonds), and structural defects [17]. For example, the authors of C. C. Yang and S. Li [18] carried out a great deal of work on the study of Raman spectra as a function of the dimensions of semiconductor nanocrystals. The results show that the Raman frequency decreases with the sizes of nanocrystallites for both narrowgap and wide-gap semiconductors. Vibrational modes associated with the change in bond lengths can shift depending on the size of the crystallites in the red region, and low-frequency deformation vibrational modes, conversely, in the blue region [19]. The red shift of Raman optical modes in particles with small dimensions is usually associated in the literature with surface tension. The amplitude of vibrations of surface atoms is always greater than in the case of atoms in the volume [20-21].

In the framework of the model of spatial correlation [22], an analysis is made of the shift and broadening of the LO line (longitudinal-optical modes) of InP nanocrystals. There was a significant

change in the spectral when the crystallite size is less than 10 nm. These changes are explained by the partial amorphization of the near-surface region of the crystals [23].

In [18], the Raman shift in TiO2 nanoparticles, caused by the effect of particle size reduction, is explained by changes in the force constants and the vibrational amplitudes of the nearest neighboring bonds. The changes are due to the effect of energy deficiency on the order of the binding energy of atoms on the surface and its effect on the force coupling constants between the uncoordinated surface atoms [24]. However, it was suggested in [25] that the observed changes in the Raman spectra with decreasing particle sizes are associated with a change in the stoichiometry and changes in the content of oxygen atoms in TiO₂ nanoparticles, rather than associated with any internal stresses or dimensional effects.

4 Conclusions

In summary, nanopowders of tungsten oxide and tungsten nanoparticles were successfully prepared by a facile and environmental method using degreased cotton as a supporter. The method makes it possible to obtain nanopowders of refractory metals at low temperatures. The structure of the synthesized samples was studied using XRD, SEM and Raman spectroscopy. The dependence of the Raman spectra and X-ray diffraction patterns on the synthesis temperature of the samples was studied. Redshift of the Raman lines and changes in their shape and intensity are induced by the increasing annealing temperature. It can be explained by the increasing crystallite sizes, which also is proved by

XRD data. An analysis of the obtained data allows to conclude that the proposed method is effective for obtaining of tungsten oxide and tungsten metal nanopowders with controlled particle sizes. Moreover, the use of degreased cotton as supporter leads to effective increase of specific surface area, which is important for electrodes in supercapacitors and catalysts.

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Synthesis and microstructure of p-type porous gallium phosphide layers

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Gallium phosphide is a semiconductor material of great interest for new modern LED technologies. Here we report the results of research on obtaining of nanostructured porous gallium phosphide layers by electrochemical etching of the monocrystalline (100) p-type GaP substrate surface. The structure and surface morphology of obtained samples were studied by scanning electron microscopy, atomic force microscopy and Raman spectroscopy. The chemical composition of nanostructured GaP surfaces was studied by energy dispersive X-ray spectroscopy, which showed that the pore formation during electrochemical etching are mostly due to dissolution of phosphorus atoms rather than gallium .It was found that shape and size of structures are strongly depending on electrochemical etching conditions. At constant applied voltage and varied current we observe that the pore size is increasing from 10 μ m to 50 μ m, and at fixed current, but varying the voltage the pore diameters can be achieved in the range between 100 to 200 nanometers.

Key words: gallium phosphide, porous structure, electrochemical etching, SEM, AFM. PACS numbers: 61.46.-w; 42.70.-a; 52.38.Bv.

1 Introduction

Among modern electronic device technologies LED is one of the fast growing in the world [1]. Porous semiconductors are of great interest because of their interesting optical properties different of those for bulk material [2-4]. Gallium phosphide and related nanomaterials are of great interest as a research object for modern LED technologies and other photonic applications [5-7]. Porous gallium phosphide (por-GaP) is a very promising material for various photonic applications [8-10]. The first reports on por-GaP obtaining and characterization are referred since 1990s [11-14]. One of the most effective ways of obtaining porous structure from the A^{III}B^V materials is electrochemical etching [15-17]. The advantages of the method are good process controllability and relative cheapness. By changing the parameters of electrochemical etching, such as current density, voltage and duration of etching, one can obtain porous structures of different morphology [18]. However, in most of reports there are description of n-type por-GaP, and the less is for p-type ones [19]. Present paper is devoted for investigation of features of p-type por-GaP layers electrochemical formation, their structure and surface morphology.

2 Experimental details

GaP films obtained Porous were bv electrochemical etching of the single crystalline, (100) oriented, p-type GaP substrate surface using electolyte containing the mixture of ethanol (C₂H₅OH) and 40% hydrofluoric acid (HF), taken in a volume ratio of 1:1. Electrochemical etching was carried out in a fluoroplastic etching cell cell. In our experiments applied voltage was varied from 30 to 65 V, current density – from 1 to 10 mA/m² and etching time - between 10-40 minutes. Figure 1 shows the schematic representation of experimental electrochemical etching process.



Figure 1 – Schematically representation of electrochemical etching process on the surface of monocrystalline GaP substrate

The microstructure of obtained por-GaP layers has been studied by scanning electron microscopy (SEM) using an ULTRA 55 FE-SEM (Carl Zeiss) microscope, and surface morphology was studied by atomic force microscopy (AFM) which measurements were provided on Integra Spectra (NT-MDT). Raman spectra of samples were measured on Solver Spectrum (NT-MDT) spectrometer in air at room temperature, excitation wavelength was 473 nm, acquisition time 30 s, and diameter of laser spot 2µm. The chemical composition of obtained surfaces was studied by Energy dispersive X-Ray (EDX) spectroscopy. Energy-dispersive X-ray spectra of samples were measured using the Bruker Quantax Flatquad.

3 Results and discussion

It us known that the process of porosity formation correlates directly with voltage, current density and etching time [20, 21]. One of the aims of our experimental study was to find up the optimal technological conditions of electrochemical etching

for p-type por-GaP structures formation. The top view SEM images of por-GaP samples, obtained under different modes of electrochemical etching are shown in Figure 2a and 2b. One can see that the structural properties of por-GaP layers are directly depend on the parameters of electrochemical etching. It is experimentally shown that the formation of a uniform porosity on the surface is observed when the etching voltage is greater than 50 V. In this case, the surface structure of the samples is uniformly flat, and pore size are almost the same. For sample shown in Figure 2a pores sizes varied from 10 to 100 nm, thus structure could be considered as a nanoporous material. In addition, structure shown in Figure 2b has more loose structure with pore sizes varied from 200 nm to 40 um. It is clear that the surface structure of samples obtained under low voltage and current intensity is non-uniform. This phenomenon can obviously be explained due to the different rate of dissolution under the influence of electromagnetic fields of different powers, which leads to dissolution of material in one (see Figure 2a) or several directions (see Figure 2b).



Figure 2 – Planar view SEM images of por-GaP surface obtained by electrochemical etching under: (a) U = 65 V, I = 10 MA, t = 15 min and (b) U = 30 V, I = 7 MA, t = 17 min

The surface morphology was also studied by atomic force microscopy (AFM) which allowed us to observe the pores size distribution on the surface of por-GaP layers. The top view AFM images of the por-GaP obtained under different electrochemical etching parameters are shown in Figure 3a and 3b. It is notable that the surface of porous layers becomes flattened after electrochemical treatment. When the etching time is longer, the surface of the sample is easily polished. The lightly polishing effect can be reached at low anodizing currents densities up to 5 mA/cm^2 , voltages up to 40 V and the etching times up to 30 minutes.



Figure 3 – AFM images of por-GaP surface obtained by electrochemical etching under: (a) U = 30 V, I = 5 MA, t = 25 min and (b) U = 40 V, I = 1 MA, t = 60 min

The method of energy-dispersive X-ray spectroscopy was used in order to identificate the elemental composition of samples. As shown in Figure 4, the basic element on the por-GaP is mainly gallium. The reason of such appearance is in the faster dissolution rate of phosphorus atoms rather the gallium ones. Since the initial substrate of crystalline p-type GaP is doped by Zn, there is also a signal of Zn appeared in EDX spectra. One can see that formation of pores during electrochemical etching process is mainly due to dissolution of phosphorus in electrolyte. Broken bonds of Ga ore passivized by oxygen. Thus por-GaP walls separating the pores are formed by GaO. Therefore, most of the porous skeletons are composed of Ga and GaO. According to data the sample also contains C, F, Zn, and Al, except of Ga, P and O elements in small amounts.



Figure 4 – Energy-dispersive X-ray spectrum of por-GaP sample obtained by electrochemical etching under U=30 V; I=5 MA; t=40 min



Figure 5 – Raman spectra of por-GaP samples obtained by electrochemical etching under different conditions

One of the linear optical methods for estimating morphology the surface and structure of nanostructures is Raman spectroscopy. In our experiments excitation wavelength was 473 nm, acquisition time was 30 s, diameter of laser spot was 2µm, enhancement factor was 100x, exciting laser power 30W. Figure 5 represents Raman spectra of the crystalline GaP and por-GaP samples obtained by electrochemical etching at different etching times. It should be note that both LO and TO oscillations modes of GaP (at 366 cm⁻¹ and 404cm⁻¹ ¹) appeared in por-GaP layers spectra. One can see that at long etching times signal has a high intensity, which shows that the structure has changed. Por-GaP sample etched for 40 minutes also has extended shoulders in Raman spectra, which shows the beginning of phase transition from monocrystalline to the amorphous phase.

4 Conclusions

Electrochemical etching method was used to obtain p-type porous gallium phosphide structures, and effective technological conditions were formed. The dependence of the structural properties of the obtained porous gallium phosphide the on electrochemical etching parameters was investigated. The uniform porosity structure formation was observed when the anodizing voltage was higher than 50 V. In such a case, the surface structure of the samples becomes evenly flat. In such modes, the effect of light polishing on surface morphology appears. Energy-dispersive X-ray spectrum of por-GaP samples shows that formation of pores during electrochemical etching process is mainly due to dissolution of phosphorus in electrolyte. Raman spectroscopy showed that the structure of the long etched (40 minutes) samples was close to the amorphous phase. The high concentration of LO- and TO-oscillations shows that the crystalline direction of the first monocrystal GaP is preserved. Obtained results can be useful in further investigations of physical and chemical properties of p-type porous gallium phosphide nanostructures for different applications in photonics and opto-electonics.

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Silicon nanocrystals: physical properties and potential biomedical applications

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Silicon (Si) nanocrystals (NCs) possess photoluminescence at room temperature and promising properties for biomedical applications as bioimaging and various therapeutic modalities. The photodynamic therapy application is based on an ability of Si-NCs to sensitize the generation of reactive oxygen species under illumination. The sonodynamic therapy with Si-NCs can be realized due to their properties to activate the cavitation followed by destruction of cancer cells and tumors. Furthermore, Si-NCs in aqueous media under electromagnetic radiofrequency irradiation can activate the heat release that is promising for the hyperthermia treatment of cancer. This paper reviews the physical properties of Si NCs, which are essential for their applications both in medical diagnostics and therapy. In the paper the properties of Si-NCs and nanoparticles (NPs) are analyzed to reveal their potential for biomedical applications. Besides the data on physical properties of Si-NCs and NPs the results of biomedical investigations of these nanomaterials are also discussed.

Key words: silicon nanocrystals, photoluminescence, bioimaging, biomedical applications. PACS numbers: 61.46.+w, 78.55.-m.

1 Introduction

Silicon (Si) is one of the most abundant elements in Earth's crust (27.7% by weight) and its crystalline form c-Si is the main functional material for modern micro- and optoelectronics. Recently, Si nanocrystals (NCs) have attracted much attention due to their physical properties and potential applications in optoelectronics, sensorics and biomedicine [1-5]. The rapid development in Si-NC applications is favorable because of their quite low toxicity and an ability to be eliminated from the body by dissolving into orthosilicic acid [6,7]. Si-NCs are proposed to be used in cancer therapy as photosensitizers [3] and sensitizers of ultrasound radiation [8, 9], high frequency electromagnetic field [10], and drug carriers [11-13]. It was shown that Si-NPs are promising for both cancer therapy and diagnostics, i.e. theranostics [14-17].

Many years ago, porous Si (por-Si) was invented and investigated as a new morphological form of silicon formed by electrochemical etching of bulk crystalline silicon (c-Si) wafers in hydrofluoric acid solutions [18]. Now it is known that por-Si formed from substrates of lightly doped p-type c-Si wafer is microporous, i.e. the mean pore size does not exceed 2 nm [19]. For high pore density, which can be achieved at certain etching microporous por-Si regime, consists of interconnected Si-NCs with average sizes varied from 1 to 5 nm, depending on the preparation conditions [20]. The quantum confinement for charge carriers in such small NC results in an increase of the energy gap [21-23]. The confinement effect is found to be strongest for spherical clusters of Si atoms, i.e. for smallest NCs with size restrictions in three dimensions [24]. Recently, chemically pure spherical Si-NCs were formed by pulsed lased ablation in inert gas or in water and various biomedical applications of the prepared NCs were proposed [16, 17].

In the present paper the properties of Si-NCs and nanoparticles (NPs) are analyzed to reveal their potential for biomedical applications. Besides the data on physical properties of Si-NCs and NPs the results of biomedical investigations of these nanomaterials are also discussed.

2 Optical absorption and photoluminescence

Due to the quantum confinement and size distribution of Si-NCs, the effective band-gap energy of por-Si ranges typically from 1.2 eV up to 2.5 eV as it was theoretically shown in Ref. [24]. Experimental data of the absorption coefficient of Si-NCs in mesoporous Si demonstrate that for the photon energy above 3 eV the main contribution to the absorption is due to the transitions above the direct gap of c-Si and then the spectrum is similar to that of c-Si [1, 2]. In this spectral range the absorption coefficient can be well described by the effective medium approximation [25]. The shift of the absorption curve to higher energies is due to reduced density and quantum confinement in Si-NCs. Only at high energies when all NCs are absorbing in the range of a high density of states this discrepancy becomes smaller and, finally, vanishes

at the energy of the direct transitions [21]. Note the absorption coefficient of por-Si shows the continuous spectral dependence (see Figure 1), which is important for the photosensitizing properties under excitation in the broad spectral range.

While the photoluminescence (PL) of por-Si is sensitive to details of the electrochemical formation and storage there are unambiguous evidences of the quantum confinement effect in Si-NCs on the PL band position [1,2]. For example, it is possible to tune the PL band position of por-Si in the spectral range from 1.1 to 2.5 eV by using different c-Si substrates and etching conditions (Fig.2). The PL properties of por-Si are also dependent on defects and contaminations, which can take place on highly developed surface of Si-NCs [1,2]. The influence of defect states on the optical and electronic properties of Si-NCs was confirmed by many experimental methods as optical absorption spectroscopy [21,24], PL and photoacoustics spectroscopy [26-28] as well paramagnetic electron resonance (EPR) as measurements [29-31].



Figure 1 – Spectra of the absorption coefficient of microporous Si (dots) and bulk c-Si (solid line) at T=300 K. Dashed line: effective medium calculations using the Bruggeman approach for 72% porosity (Ref. [21])



Figure 2 – PL spectra of por-Si prepared with various etching parameters. The arrow indicates the spectral position of the lowest energy free exciton transition in c-Si (Ref. [21])

It is established that the Coulomb interaction between photoexcited electrons and holes in a small Si-NC influences strongly their energies and then the PL spectrum [23,24]. The attractive Coulomb interaction for charge carriers in the Si-NC results in a formation of excitons with relatively large binding energies of about hundreds of meV, which determine possibilities for the excitons to be stable at room temperatures [22]. Furthermore, the exchange interaction in an exciton can remove the spin degeneracy for the exciton states. It results in two possible spin configurations for the exciton in Si-NCs, which consist of optically active spinsinglet states and optically inactive spin-triplet ones. The triplet exciton state is lowered in energy in respect to the singlet state because of the electronhole exchange interaction [23]. Despite a small singlet-triplet splitting being in the range from 1 to 30 meV the main part of excitons (75%) reside in the threefold degenerated triplet state even at elevated temperatures [21].

3 Photosensitizing properties

Singlet oxygen $({}^{1}O_{2})$ is known to be an excited form of molecular oxygen (O₂), which mediates important biochemical processes in living organisms [32]. The biochemical reactivity of ${}^{1}O_{2}$ is used in socalled photodynamic therapy (PDT) of cancer, which is based on a combination of photoactive drug and light treatment of tumors [33]. According to the quantum mechanics the relaxation of singlet states back to the ground (triplet) state is "spin forbidden" and thus ¹O₂ is characterized by rather long lifetime [35], which is favorable for transferring the excess energy to another molecule. The most useful in biomedical applications and widely used procedure of the ${}^{1}O_{2}$ generation is a photosensitization, which includes a certain "photosensitizer", substance called e.g. dye molecules [34, 35]. It was found that Si-NCs in asprepared por-Si were able to photosensitize the ${}^{1}O_{2}$ observed generation [36]. The efficient photosensitization was explained by the energy transfer from excitons in Si-NCs to O₂ molecules adsorbed on the surface of Si-NCs [37]. This process is favorable because of highly developed surface area of the order of $10^2 \div 10^3$ m²/g of small Si-NCs [19,20] and long radiative lifetimes (10⁻ $5 \div 10^{-3}$ sec) of excitons confined in the Si-NCs [21].

A quenching of the exciton photoluminescence (PL) of Si-NCs in por-Si with adsorbed O₂ molecules was used to clarify the energy transfer mechanism [37,38]. While the PL quenching is only an indirect evidence of the ${}^{1}O_{2}$ formation, the direct and quantitative data can be obtained by analyzing the radiative decay of ¹O₂ molecules at 0.98 eV [37,39]. $^{1}O_{2}$ (1270)nm) In fact. the photosensitization by Si-NC was quantified by means of the luminescence spectroscopy at 0.98 eV

[37]. On the one hand, a lot of the experiments on the ¹O₂ luminescence demonstrates the efficient generation of ¹O₂ by the energy transfer from Si-NCs [36]. On the other hand, a comparison of the ¹O₂ luminescence intensity for Si-NCs and for the standard photosensitizers as porphyrins gave a strong evidence of a deactivation (quenching) of ${}^{1}O_{2}$ molecules in Si-NC structures [40], which limits significantly the net concentration of ¹O₂ sensitized by Si-NCs. The EPR technique can provide information about the $^{1}O_{2}$ concentration in different reactions [34, 35]. The X-band EPR spectroscopy of photoexcited Si-NCs in O2 atmosphere gave estimates of the concentration of photosensitized ¹O₂ molecules to be about $10^{18} \div 10^{19}$ cm⁻³ under excitation with photon flux of about $10^{19} \div 10^{20}$ cm⁻² [30,31]. The ${}^{1}O_{2}$ photosensitization was observed for por-Si NPs dispersed in different oxygen-saturated organic and inorganic liquids [38] as well in water [39]. Furthermore, the biomedical experiments in vitro demonstrated an effect of the strong suppression of the cancer cell proliferation by introducing photoexcited por-Si NPs [3].

The first evidence of the photosensitized property of Si-NCs was observed at cryogenic temperatures [5, 6]. The investigated samples of por-Si were prepared by standard electrochemical etching of (100)-oriented boron-doped c-Si wafers with a resistivity of 10-20 Ω^* cm in a solution of hydrofluoric acid. he prepared free standing por-Si layers were dried in air for several hours. Then, the prepared layers were milled to get powder assembled from por-Si NPs and their agglomerates. The powder was kept in a vacuum chamber in oilfree vacuum with a residual pressure of about 10⁻⁵ Torr. The exciton PL spectrum of por-Si measured in vacuum at low temperature is characterized by a broad, featureless emission band located in the visible region (dashed line in Figure 3). The spectral position and bandwidth reflect the wide band-gap distribution of the Si-NC assembly. Intrinsic defects as Si dangling bonds [31] seem to be responsible for the infrared PL band below 1 eV [21]. The adsorption of O₂ on the surface of Si-NCs resulted in a strong suppression of both the exciton PL and

the defect PL band (solid line in Figure 3). The PL quenching by O₂ adsorption is maximal for the PL photon energies above 1.63 eV. The latter value corresponds to the ${}^{3}\Sigma \rightarrow {}^{1}\Sigma$ transition energy in O₂ molecule. At the same time the PL line at 0.98 eV, which is related to the radiative transition ${}^{1}\Delta \rightarrow {}^{1}\Sigma$, appeared after oxygen adsorption on Si-NCs (see inset in Figure 3). These spectroscopic data give direct evidences of the ${}^{1}O_{2}$ photosensitization by Si-NCs. Detailed description of the energy-transfer mechanism responsible for the photosensitized generation of ${}^{1}O_{2}$ by Si-NCs can be obtained from the spectral dependence of the PL quenching strength, which can be defined as follows [36]:

$$Q = I_{PL}^{vac} / I_{PL}^{ox}, \tag{1}$$

where I_{PL}^{vac} and I_{PL}^{ox} are the PL intensities of Si-NCs in vacuum and in oxygen ambient, respectively. The efficiency of the energy transfer from excitons in Si-NCs to O₂ molecules can be obviously calculated by using the following expression [28]:

$$\eta = l - Q^{-l}.\tag{2}$$

The spectra of $Q(hv_{PL})$ and $\eta(hv_{PL})$ demonstrate both the main maximum at 1.63 eV (Q >> 1, $\eta \sim I$) and an additional maximum at hv_{PL} of about 57 meV below the $^{1}\Delta$ state energy as well as numerous maxima separated by energy of about 63 meV [36, 37]. These maxima correspond to the energy transfer from Si-NCs with band gaps, which do not match resonantly the excitation energies of the singlet states of O_2 . A local maximum separated by 57 meV from the main maximum at 1.63 eV is an evidence of the indirect radiative transition in Si-NCs where the participation of the momentum conserving TO phonon with energy of 57 meV is required [21]. The excess of the exciton energy with respect to the energies of the $^{1}\Delta$ and $^{1}\Sigma$ states is released the emission of TO phonons with energy of 63 meV [36].



Figure 3 – PL spectra of por-Si in vacuum (dashed line) and in the presence of adsorbed oxygen molecules (solid line). Transition energies from the excited states $({}^{1}\Delta, {}^{1}\Sigma)$ of ${}^{1}O_{2}$ to the ground state are indicated by dashed vertical lines. Spin configurations and spectroscopic labeling of molecular oxygen states are shown. Inset depicts the PL line related to the ${}^{1}\Delta \rightarrow {}^{1}\Sigma$ transition in O₂. Temperature T=5 K, excitation at 2.41 eV (Ref. [37])

The dynamics of the energy transfer can be deduced from the PL transients of Si-NC in the presence of adsorbed O2 molecules. The energy transfer time from one Si nanocrystal to a single O₂ molecule is not accessible experimentally, since a large number of Si-NCs contributes to the PL at certain emission energy. At low temperatures in vacuum the PL decay times, τ_{PL} , is approximately equal to the radiative lifetime of excitons in Si-NCs, τ_{ex} , and it is about ~10⁻³ s independently on the PL photon energy [21]. The PL quenching by O_2 adsorption is accompanied by a significant decrease of the PL decay time because the adsorbed O_2 molecules on the Si-NC surface represent a channel for the nonradiative recombination of the excitons. The spectral dependence of τ_{PL} follows the quenching strength spectrum. The shortest τ_{PL} is observed for the Si-NCs, which transfer their excitation most efficiently [36, 37]. Increasing the concentration of adsorbed O2 molecules results in a stronger PL quenching and further decrease of τ_{PL} [37]. The time resolved PL studies performed with nanosecond time resolution confirmed this spectral behavior of the exciton lifetimes of Si-NCs in oxygen ambient (see Figure 4).

Besides the quenched exciton PL in por-Si with adsorbed O₂ molecules there are infrared PL bands related to defects in Si-NCs and radiative transitions in the photosensitized ${}^{1}O_{2}$ (see Figure 3). The relevant time scale of the infrared PL was determined from time-resolved measurements. Inset of Figure 4 shows the transients of the defect-related emission for por-Si in vacuum detected at the photon energy of 0.953 and 0.973 eV. The rise time coincides within the response time of the used experimental setup (~100 ns) and yields an upper limit for the time of carriers capture to defect states [21]. The nonexponential decay proceeds on a microsecond time scale and does not vary with PL photon energy. In the presence of adsorbed O₂ molecules the radiative decay of the ${}^{1}\Delta$ state of ${}^{1}O_{2}$ is observed at detection energy of 0.953 eV. The initial fast decay is attributed to the defect-related PL background. The slow component with the lifetime $\tau_{\Lambda} \approx 0.5$ ms accounts for the $^{1}\Delta \rightarrow ^{3}\Sigma$ transition in O₂. This lifetime is significantly shorter

that the radiative lifetime of a free O_2 molecule due to the interaction with Si-NCs. The same interaction should also influence the radiative lifetime of adsorbed 1O_2 molecules. Firstly, the quantum yield $\eta_r \approx 7 \cdot 10^{-5}$ of the radiative decay of the ${}^1\Delta$ state is estimated from the comparison from the integral intensity of the exciton PL band. Then $\tau_r \approx 7$ s is obtained by using the simple relation $\tau_r = \tau_{\Delta}/\eta_r$. On the one hand, the obtained τ_r is much shorter than the undisturbed radiative lifetime of about 50 min [34]. On the other hand, $\tau_r \approx 7$ s is close to the radiative lifetimes of ${}^{1}O_2$ in different solvents [35]. Therefore, Si-NCs act as both the photosensitizer and a quencher of ${}^{1}O_2$.



Figure 4 – Transients of the infrared PL of ${}^{1}O_{2}$ (detection energy E_{det} =0.973 eV) and defect-related PL at hv_{PL} =0.953 eV of por-Si with adsorbed O_{2} molecules at T=5 K. Inset: PL transients of the defect-related PL of por-Si in vacuum (Ref. [37])



Figure 5 – Spectra of the room temperature PL of por-Si in vacuum (1), in oxygen ambient at *p*=760 Torr (2) and just after evacuation (3). Inset shows the spectrum of the energy transfer (Ref. [28])

While the above discussed PL experiments at cryogenic temperatures are important to clarify details of the photosensitization of ¹O₂ by Si-NCs, the $^{1}O_{2}$ generation at room temperature is of most practical interest. Contrary cryogenic to temperatures, the optimal interaction conditions for Si-NC/O₂ system are not fulfilled at elevated temperatures. Because of the thermally activated desorption a small spatial separation is realized only during a short time of collisions between O₂ molecules and Si-NC's surface. Additionally, the exciton lifetime and the occupation number of the spin-triplet state of the exciton decrease with rising temperature [21]. It results in a weaker PL quenching, which scales with the collision rate, i.e., the gas pressure [37], and in a broad spectral resonance of the energy transfer to the 1Σ state as it is shown in Figure 5. The corresponding spectrum of η is presented in the inset of Fig.5. On the one hand, the maximal value of $\eta \approx 0.7$, which occurs at 1.63 eV, indicates the rather efficient energy transfer from excitons in Si-NCs with resonant energies to O_2 molecules. On the other hand, the spectrally averaged efficiency of the energy transfer for por-Si, which can be obtained by simple integration of $\eta(hv_{PL})$, does not exceed 0.5. Taking into account that the quantum efficiency of the exciton PL is typically smaller 10%, one can estimate the quantum efficiency of the ${}^{1}O_{2}$ generation at room temperature to be lower 5%. Note, the dependence of the ${}^{1}O_{2}$ generation efficiency on the O_{2} ambient pressure at room temperature is well described by the Langmuir approach for molecule adsorption [28]. The good agreement between the experimental data and Langmuir model indicates that the amount of the photosensitized singlet oxygen is almost proportional of the number of adsorbed oxygen molecules. This fact has to be taken into account for different applications of the photosensitizing properties of Si-NCs.

Besides the characteristic energy of about 1.63 eV (the ${}^{1}\Sigma \rightarrow {}^{3}\Sigma$ transition energy in O₂ molecule), the spectrally selective quenching of PL intensity of por-Si can demonstrate an additional maximum at photon energy of about 2-2.2 eV (see inset in Fig.5). The high energy quenching maximum is usually observed for por-Si samples with a broad

distribution of Si-NCs sizes and surface conditions, e.g. for por-Si powders obtained by mechanical grinding of por-Si films or by stain etching of polycrystalline Si powder [39]. The origin of the high energy quenching can be related to the formation of superoxide radicals, i.e. O_2^{-} [35]. There are no unambiguous evidences of this characteristic energy of the O_2^{-} formation. But the latter process is known to be more energy consumed than the ¹O₂ generation. The PL quenching at 2-2.2 eV can be also explained by the charging of Si-NCs due to the O_2^{-} formation on the Si-NC's surface. The positively charged volume of Si-NCs results in an increase of the nonradiative Auger recombination [28].

Additional information about the ${}^{1}O_{2}$ photosensitization at room temperature is obtained from the PL transient measurements. Figure 6 presents several PL transients of por-Si in gaseous oxygen ambient [37]. The PL transients are not actually mono exponential (see Figure 6). However, for longer times (typically, >50 µs after the excitation laser pulse) they can be approximated by the exponential function as follows:

$$I_{PL}(t) = I_{PL}(0) \exp(-t/\tau_{PL})$$
 (3)

where τ_{PL} is the mean PL lifetime, and $I_{PL}(0)$ is the PL intensity just after excitation. The values of τ_{PL} for the samples in vacuum are found to be about tens microseconds that is in good agreement with the singlet lifetimes of excitons in Si-NCs [21].

The admission of O_2 causes a decrease of τ_{PL} and this effect is stronger at higher oxygen pressure (see Figure 6). The strongest lifetime shortening occurs at the PL energy of 1.6 eV, which correlates with the spectral maximum of the PL intensity quenching. The PL lifetime shortening after oxygen adsorption was nearly reversible at low oxygen pressure [28]. The detailed analysis of the PL transients indicates that the singlet oxygen-induced defect formation results mainly in a decrease of the number of luminescent Si-NCs. It can be understood by taking into account the short lifetime (<1 µsec) of the nonradiative recombination of photoexcited charge carriers in Si-NCs with dangling bonds [36].



Figure 6 – Transients of the room temperature PL at 1.63 eV of por-Si in vacuum (1), in oxygen ambient at *p*=760 Torr (2) and just after evacuation (3)

Due to the fast nonradiative relaxation of ${}^{1}O_{2}$ in water [35] it is practically impossible to detect the ${}^{1}O_{2}$ luminescence in aqueous solutions. In this case the ${}^{1}O_{2}$ photosensitization can be indirectly probed by monitoring the intensity and lifetime of the exciton PL of Si-NCs. Figure 7 shows typical PL spectra of por-Si powder dispersed in oxygensaturated water and in water after O₂ degassing. One can see that O₂ dissolved in water caused the spectrally selective PL quenching (inset in Figure 7). Although the PL quenching strength in water is weaker, its spectral shape is similar to that measured in gaseous O_2 ambient. Note that the relative contribution of the high-energy quenching at 2-2.2eV is stronger for por-Si in water than for the case of gaseous ambient. It implies that the Si-NCs charging or/and O_2^- formation is more efficient in presence of polar molecules of water, which can decrease barriers for the charge trapping on the Si-NC's surface.



Figure 7 – Spectra of the room temperature PL of por-Si in water without (1) and with dissolved oxygen at p=760 Torr (2) and just after O₂ degassing (3). Inset shows the spectral dependence of the efficiency of energy transfer

The lifetime of the exciton PL of por-Si NPs dispersed in water was found to decrease after saturation of the solution by O_2 . The energy transfer times can be determined from transients of the

exciton PL [28]. The spectral dependence of the energy transfer time was found to be similar to that in gaseous oxygen ambient. A slightly longer energy transfer time correlates with weaker quenching of

the PL intensity of por-Si in water than that in gaseous O_2 . This fact indicates an influence of water molecules on the exciton recombination and/or energy transfer from the excitons to O_2 molecules. Indeed, the energy transfer is mostly efficient for Si-NCs with hydrogenated (H-terminated) surfaces, which are hydrophobic [19]. Therefore, Si-NCs dispersed in water should be partially oxidized that results in decreasing the 1O_2 photosensitization efficiency [37].

The oxidation of Si-NCs in air or in aqueous solutions seems to be the main limiting factor to achieve the stable and efficient photosensitization of O_2 generation [39]. The oxidation process can be also enhanced by 1O_2 photosensitized by por-Si [38]. In order to overcome this serious limitation for the application of Si-NCs as efficient photosensitizer of 1O_2 it is probably required a special procedure of controllable oxidation and/or surface modification of Si-NCs. It can be done, for example, by using rapid thermal annealing or laser irradiation.

The above discussed efficient photosensitization of ¹O₂ by Si-NCs in different ambiences stimulates experiments on biomedical verification for the expected photodynamic action. It was found that photoexcited por-Si NPs, which consisted of aggregated Si-NCs, could suppress the proliferation (permanent division) of cancer cells [3]. For these biomedical experiments Si-NCs were prepared by using the conventional method of the electrochemical etching of c-Si wafers in hydrofluoric acid solutions [19]. The obtained freestanding por-Si films were dried in air and then milled to get a powder of por-Si NPs. According to the Raman scattering data, the mean sizes of Si-NCs in the initial por-Si layers and in the powder formed from them were about of 3-4 nm. Then the por-Si powder was dispersed in pure water bubbled with oxygen to get a homogeneous aqueous suspension. It was found that the exciton PL intensity of Si-NCs in oxygen-saturated water decreases by 1.5-2 times in comparison with that in oxygen-free water [3].

Additional information on the ¹O₂ photosensitization efficiency was obtained by

analyzing PL transients at 1.63 eV of Si-NCs excited by laser pulses. The relaxation time of the exponential part of the PL transients in the solution without O₂ was $\tau_{ex} \approx 85 \ \mu$ s, which is close to the natural radiative lifetime of excitons confined in Si-NCs. The saturation of the solution with gaseous O₂ at a pressure of 760 Torr leads to a decrease in the PL dacay time to $\tau_D \approx 50 \ \mu$ s. The ratio $\tau_{ex}/\tau_D \approx 1.6$ is close to the measured PL quenching. These observations indicate that the decrease of the PL lifetime of Si-NCs in oxygen-saturated suspensions was mainly caused by the photosensitized generation of ${}^{1}O_{2}$.

The biomedical experiments in vitro were carried out by using cancer cells of 3T3 NIH (mouse fibroblast) grown by standard procedure of their sub cultivation in the Dulbecco-modified Eagle's medium using 96-well plates or dishes. The cells were cultivated for 1.5 days, and then the medium was changed on the fresh nutrient solution with different concentrations of Si-NCs. One part of the wells was illuminated by mercury lamp, another part was kept in darkness and some cells were used for control (without Si-NCs and illumination). The inhibitory or lethal effect of the illumination was obtained by measuring the cell quantity in nonilluminated and illuminated wells per cells quantity in the control wells in which the Si-NC suspension was not added. Dependence of the cancer cell number (relative to the control) as a function of the concentration of por-Si powder in the solution is given in Figure 8. The number of survived cells after the irradiation in the growth medium with Si-NCs concentration about 0.5 g/l decreases strongly as compared to the reference group. The death of 80% of cells was detected for the concentration higher 2 g/l. At the same time, the effect of por-Si was almost absent over the entire concentration range in darkness. This fact is concerned with the $^{1}O_{2}$ generation process under the illumination in the active solution with dispersed Si-NCs, because ¹O₂ being strong oxidizing substance results in both killing of cells and the inhibitions of cell proliferation.



Figure 8 – Number of cancer cells in darkness (1) and after illumination (2) vs Si-NCs concentration in nutrient solution (Ref. [3])

The detected death of cancer cells occurred due likely to the action of photosensitized active oxygen, in particular, to the oxidation of cell substance by ${}^{1}O_{2}$. In addition, the effect of other active forms of oxygen as superoxide (O_{2}^{-} ions) was also possible [3]. To reveal the particular mechanisms of the interaction between photoexcited Si-NCs and biological objects, additional investigations are still required.

4 Sensitization of therapeutic ultrasound

Sonodynamic therapy (SDT) is a method of mild cancer therapy, which is realized by using ultrasonic irradiation (USI) with therapeutic intensity in the range of 1-10 W/cm² [8]. SDT usually requires more simple and cheap set-up in comparison with other methods based on high-intensity focused ultrasound [41]. NPs of por-Si were successfully used as sonosensitizers under USI at 37 kHz for the destruction of cancer cells in vitro [42,43]. It was found that the NPs activated by USI with relatively low intensity about 0.2 W/cm² did not destroy directly the cells, while the cell death occurred for 1-2 days due to the apoptosis. In order to explain the observed effect, the possible mechanisms of the cell death were proposed: (1)local heating (hyperthermia); (2) "nano-scalpel" effect of NPs, which destroy mechanically the cancer cells; (3) sensitization of cavitation, which results in the shock wave generation and additional dissipation of the ultrasound energy [43]. Note, that the USI with frequency in the kHz range is usually accompanied

by strong cavitation and the third mechanism should be dominant. However, the therapeutic USI is commonly operated at the MHz frequency and all the mechanisms can be important for the sonosensitizing properties of por-Si NPs.

Numerical simulations and physical experiments showed that por-Si NPs with sizes above 100 nm can efficiently sensitize the hyperthermia under therapeutic USI with frequencies of 1–2.5 MHz and intensities of 1–20 W/cm² [9]. It was noted that the dry-ground por-Si NPs exhibited 2 times larger heating than the wet-ground ones and the effect was explained by the large sizes of the former, as well as by hydrophobic properties of their surfaces and, as a consequence, greater viscous friction [9].

USI with frequency at 0.88-2.64 MHz and por-Si NPs with sizes about 100 nm were used to destroy cancer cells in vitro and in vivo. Photoluminescent por-Si NPs, which were composed by smaller Si-NCs covered with biopolymer (dextrane), were efficiently up-taken by cancer cells without any undesired cytotoxic effect in vitro. The uptake of NPs was monitored by using the PL imaging technique [8]. Furthermore, the NP suspensions with doses up to 30 mg/kg could be easily intravenously injected in vivo. It was found that the combined impact of NPs and USI with intensity of 1-2 W/cm² resulted in a strong suppression of the cancer tumor growth as shown in Figure 9 [8]. The observed SDT effect is explained by the both cavitation-induced destruction of cancer cells and local hyperthermia caused by the therapeutic USI and sensitized by Si NPs.



Figure 9 – (a) Schematic image of the experimental setup for USI experiments *in vivo*.
(b) Dynamics of the cancer tumor growth for mice with intravenously injected dextrane-coated por-Si NPs followed by USI treatment (red down triangles), for mice with intravenously injected por-Si NPs only (green circles), for mice with the USI treatment only (blue up triangles), and for the control group of mice (black squares).
The horizontal dashed line indicates the doubled tumor volume. (Ref. [8])

5 RF-induced hyperthermia

Recently, Si-NCs and NPs were found to act as efficient sensitizers of electromagnetic radiofrequency (RF) radiation-induced hyperthermia [10]. Due to a large penetration depth of the RF radiation the effect seems to be very promising to treat malignant tumors and even individual cells in The principle of metastases. **RF-induced** hyperthermia sensitized by Si NPs is shown schematically in Figure 10a.

The physical experiments showed that heating of aqueous suspensions of PSi NPs by tens of Celsius degrees could be achieved under RF irradiation at 27 MHz with relatively low intensity below 5 W/cm² (see Figure 10b). The heating effect was demonstrated for por-Si NPs prepared by mechanical grinding of por-Si layers [8] as well as for non-porous Si NPs synthesized by laser ablation of c-Si in water [16]. The observed RF heating effect can be explained by considering the polarization of Si NPs and electrolyte in the field of RF radiation electrical and the corresponding release of the Joule heat. The polarization of electrolyte ensures relatively high ionic conductivity due to the electric current outside NP, *I*_{out} (see Figure 10a). The higher heating rate for laser-ablated NPs is related by their smaller sizes. The size-dependent specific heating rate per a mass unit of NPs can be estimated by the following expression:

$$S \sim E^2 / D^2 , \qquad (4)$$

where *E* is the amplitude of the RF electrical field and D is the size of NP [10]. It was theoretically shown that the RF heating by the electrical current inside small NP, I_{in} , is weaker in comparison with I_{out} because of the significantly larger volume for the heat generation by the latter [44].

In-vivo experiments with mice under therapeutic RF irradiation were carried out (see Figure 11). The RF setup consisted of a medically approved source at 27 MHz (Figure 11a). Histology images of tumor areas, which were obtained 1 h and 3 days after the PSi NP injection and RF-based treatment, respectively, indicate both the destruction of cancer cells (visible as dark blue spots) and biodegradation of por-Si NPs in the cells (indicated by red arrows in Figure 11b-c). It was found that NPs under activation with RF radiation resulted in 35-40% suppression of the tumor growth, while NPs themselves can slightly inhibit the tumor growth (Figure 11d). This effect is explained by the toxic effect of free radicals (dangling bonds) from the surface of Si NPs during the dissolution process. Similar slight inhibition of the tumor growth took place under the action of RF radiation alone. However, the combined action of PSi NPs and RF excitation could drastically amplify the effect leading to a much stronger inhibition of the tumor growth.



Figure 10 – (a) Schematic image of the RF-radiation induced electrical currents inside and outside a Si NP and transients of the temperature growth under RF-irradiation of aqueous suspension of por-Si NPs (red circles) and pure water (black circles); inset shows the NP suspension (Ref. [10])



Figure 11 – (a) Schematics of the RF radiation-based therapy setup where (1) is a RF radiation source, (2) are the RF electrodes, (3) is a mouse having a tumor area.
(b), (c) Histology images of a tumor area 1 h and 3 days after the PSi NP injection and RF-based treatment, respectively. (d) Inhibition of the tumor growth after the following treatments: injection of PSi NPs suspension without RF irradiation (black curve);
diation 2 min without PSi NPs (blue area) injection of PSi NPs followed by 2 min BF irradiation (red area).

RF irradiation 2 min without PSi NPs (blue curve); injection of PSi NPs followed by 2 min RF irradiation (red curve); injection of a suspension of laser-ablated (LA-Si) NPs followed by 2 min RF irradiation (green curve). (Ref. [10])

6 Conclusions

The obtained results and their analysis indicate that Si nanocrystals and nanoparticles are promising sensitizers of the cancer therapy based on the photosono- and radiofrequency irradiations. The photosensitization of singlet oxygen generation occurs because of the energy transfer from photoexcited Si nanocrystals to oxygen molecules adsorbed on the nanocrystal surfaces. The singlet oxygen generation was observed for por-Si in different gaseous and liquid ambiences. The effect of photoexcited Si nanocrystals on the cancer cell proliferation was confirmed in vitro. While these observations open a way for in vivo experiments and then to possible applications of por-Si in PDT of malignant tumors, the real progress in this direction is still insignificant. The investigation of physical processes and biomedical experiment in vitro and in vivo show the good prospect of biocompatible and

biodegradable Si nanoparticles for the application in sonodynamic therapy of cancer. The RF hyperthermia sensitized by Si nanoparticles represents the mild method of cancer therapy. Moreover, the sensitizing properties of PSi NPs can be combined with cancer diagnostics by means of the optical bioimaging. These remarkable properties of Si nanoparticles are very important for implementation their practical in cancer theranostics.

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Optimal geometrical parameters of porous layer in silicon solar cells

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In the present work we have proved theoretically and experimentally that porous silicon layers with optimal thickness can be effectively used as anti-reflection coatings in solar cells and panels. In our work we have taken into account joint mechanisms of generation and recombination of free electrons and holes in porous silicon films stimulated by photons. Experimentally these films have been grown by method of electro-chemical etching. Regularities of morphology of surfaces of the films have been investigated by use of scanning electron microscopy. Results of scanning electron microscopy, measuring of short-circuit current, open circuit voltage, and values of etching time necessary for growth of the films with required characteristics have shown that in case value of thickness of the porous layer is approximately equal to two thirds of electron diffusion length, than efficiency of the solar cell with porous layer increases by 30% in comparison with the corresponding value in the absence of texturing.

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1 Introduction

Renewable resources are the so called green energy sources that provide smaller impact to external environment than conventional energy sources. Because of this transformation of solar energy into electrical energy is an important scientific and technical problem related to perspective directions of future energetics.

Solar cells and panels as usual have relatively small efficiency. Because of this it's important to reduce reflectance of photons from surfaces of the solar cells for maximization a number of photons absorbed by a semiconductor surface to convert energy of incident light into electrical energy. So, since middle of the last century, methods for separation of electrons and holes in doped semiconductors, heterostructures, and various chemical compounds due to photon action of is an important research problem [1-9].

Among the great variety of methods used for increasing of solar cells efficiency, we can distinguish a method of texturing of their surfaces used for reducing of photon reflection [10-16]. As usual, for texturing of surfaces of silicon solar cells can be used acid texturization, reactive ion etching, and mechanical texturization [17-19]. Using of method of electro-chemical etching let us construct a solar cell as films with porous surfaces, for example, porous silicon (por-Si) with pore sizes about $10-10^3$ nm [20, 21]. Porous silicon is a nanostructured material attracting considerable attention of scientists because of its unique electrical and optical properties.

Changes in morphology of the films by texturing provide an antireflection effect (about 10%), and give a possibility to increase efficiency of the solar cell in the same order. Obviously, these data are average. Resulting photoelectromotive force in the films depends on combination of many physical and geometric factors such as mechanisms of electrons and holes generation and recombination in semiconductors, wavelength of an effective part of solar radiation spectrum, topological and metric characteristics of porous layers. It's natural to expect existence of optimal sets of parameters characterizing these factors. We do not know the purposeful studies in this direction, although many experimental facts about the role of individual parameters are known. Universal recommendations for choosing of an optimal set of parameters can be obtained as a result of integration of theory and experiment.

Aim of the present work is theoretical estimation of thickness of porous silicon layer located above pn-junction necessary for maximal electron generation due to photons action with taking into account recombination of electrons and holes, as well as comparison of theoretical results with experimental data.

2 Theory and experiment

A doped layer of *n*-type semiconductor contains nanosize pores decreasing reflection of photons with energy $\hbar w$ and wavelength λ . Diameter (d), pore height (x) defined according to front-face area, and distance between them (l) have the same order as λ . This leads to realization of antireflection effect. Thickness of the porous level L must be approximately equal to diffusion length of current carriers L_D , i.e. to the distance in which their concentration decreases significantly (in *e* times). In case $L > L_D$, number of redundant electrons knocked out by photons is small. In case $L > L_D$, number of electrons recombined with holes is big. So, the problem is in determination of a relative distance x/L_D describing balance of these two effects. As usual, diffusion length L_D is estimated as

$$L_{\mathcal{A}} = \sqrt{Dt} , \qquad (1)$$

where D is coefficient of diffusion of current carriers in a certain semiconductor, t is their lifetime. It's more convenient to estimate L_D via the Debye radius as

$$L_D = \frac{V_T}{w_0} = \sqrt{\frac{kT\varepsilon}{Ne^2}} = 4,9\sqrt{\frac{eT(^{\circ}K)}{N(cm^{-3})}}, \quad (2)$$

where V_T is thermal velocity of current carriers, w_0 is frequency of free oscillations of electrons, N is concentration of extra charge carriers, e is elementary electronic charge, ε is relative dielectric permittivity of a medium, T (${}^{o}K$) is absolute temperature.

 $\varepsilon = 1$ for air inside of pores, $\varepsilon = 11,8$ for silicon. Number of redundant electrons and holes generated per second in a unit volume of a semiconductor by a photon with energy $\hbar w$ can be expressed as

$$N = \beta W / \hbar w, \ \hbar w \ge E_g, \qquad (3)$$

where W is power of solar radiation in a bulk layer with sufficient thickness equal to 1/4 of optical wavelength $\lambda = wc/(2\pi\sqrt{\varepsilon})$ corresponding to maximal photon absorption, E_g is bandgap of the semiconductor, β is quantum efficiency.

Diffusion length is a measurable physical parameter with size about a micron. So, it's necessary to define x_*/L_D , where x_* is optimal thickness of porous layer.

Number of electrons N in a surface layer with thickness $\lambda/4$ can be defined via Eq. (3). Let us consider variations of N(x) along the *p*-*n*-junction. Number of electrons generated due to photon influence is proportional to pores height x:

$$N_g = gpx\hbar w, \quad 0 \le p \le 1, \tag{4}$$

where g is generation factor of electrons along x direction, p is porosity of the film.

Number of recombined pairs consisting of electrons and holes is proportional to variations of p and x:

$$N_z = zp(1-p)x(L_D - x), \qquad (5)$$

where z is recombination coefficient.

Joint probability of realizing of two independent statistical processes of generation and recombination is

$$P(N_g, N_z) = \frac{gzp^2(1-p)}{N^2} \hbar w x^2 (L_D - x).$$
(6)

Maximum condition of $P(N_g, N_z)$ on p and x can be given as

$$\frac{\partial P(N_g, N_z)}{\partial x} \Big|_{x=x_*} = 2x_* (L_D - x_*) - {x_*}^2 = 0,$$

$$x_* = \frac{2}{3} L_D, \qquad (7)$$

$$\frac{\partial P(N_g, N_z)}{\partial p}|_{p=p_*} = 2p_*(1-p_*) - p_*^2 = 0,$$

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$$p_* = \frac{2}{3}.$$
 (8)

Optimal thickness of porous level is 2/3 of diffusion length for electrons at porosity is equal to $p = p_* = 2/3$.

At more detailed analysis we must take into account that porosity p depends of length of pores, i.e. p = p(x). Because of this we can consider Eqs. (8) and (9) as a system of interacting equations. Dependence p = p(x) can be specified theoretically via relation between lacunarity (filling of space) 1-pand fractal dimension of porous level. At $x \gg y \approx z$ (y, z are lateral sizes of pores) we have $\gamma = D - d \ge 0.1$ (D and d are fractal and topological dimensions, correspondently). Dependence p(x) is relatively weak. These singularities are typical for porous semiconductor films.

Let us consider a possibility of experimental observation of the regularity described by Eq. (7). Measurement of porosity of nanostructured films and verification of Eq. (8) represent a standing along experimental problem.

For our experiments we used a *p*-type monocrystalline silicon film. Thickness of this film was 350 micrometers, resistivity was 12 Ohm cm, *p*-*n*-junction was formed by use of thermo-diffusion of phosphorus. Thickness of n^+ -layer was about 700-1500 nm and comparable with electron diffusion length. Because of this after etching the film contains pores with sizes smaller than distance to *p*-*n*-junction. Scheme of a solar cell based on porous silicon is shown in Figure 1.



Al contact

Figure 1 – Scheme of a solar cell based on porous silicon

The silver-aluminum contact was obtained by deposition of metallic Ag. Porous silicon was obtained by electrochemical anodizing of surface of n^+ -layer at different values of current density and etching time. Electrochemical anodizing was fulfilled in electrolyte *HF*: ethanol in the ratio 1:1 at anodizing current density 20 mA/cm².

Increasing of anodizing current density and etching time lead to increasing of thickness of porous layer in direction to the plane containing *p*-*n*-junction. In order to find an effective thickness of silicon porous layer x_* corresponding to maximal value of short-circuit current of the solar cell we

used etching of diffusion *n*-layer of the solar cell with different time durations.

We obtained images of micro-structure of crosssection of porous silicon near the *p*-*n*-junction. For this aim we used a scanning tunneling microscope (SEM). In order to better visualize of porous structure layers of *p*-*n*-junction we used a high concentration solution HF and bright illumination from tungsten lamp of the end face of the sample.

Figure 2(a) demonstrates SEM-image of crosssection of porous silicon obtained at short time used for etching of n-layer. Figure 2(b) corresponds to long-term etching time.



Figure 2 – SEM-images of cross-section of solar cell with porous silicon film

SEM-images contain areas of *p*-*n*-junction, *n*-layer (thickness is 1,5 mkm) and porous silicon layer (thickness is 903,8 nm) of the solar cell.

We measured values of short-circuit current $I_{sh.c.}$ in porous layer at illumination of tungsten incandescent lamp with power 87 mW/cm². Also we defined open-circuit voltages and the duty cycle of the volt-ampere characteristic of the solar cell. At first, the output parameters of polished solar cell without a porous layer were measured. Then we measured these parameters for silicon films with different thickness of porous layer. Figure 3 confirms the existence of effective thickness of porous level corresponding to maximal value of short-circuit current density of the solar cell. Location of nanopores was defined from the SEM images shown in Figures 2(a), (b). Maximal short-circuit current 22,1 mA/cm² in *n*-layer of the solar cell corresponds to etching time 10 sec and thickness of porous level 420 nm. Value of short-circuit current increases by 30% of its initial value measured in case of absence of the porous layer. Changing of solar cell efficiency with increasing of thickness of porous *n*-layer in the direction of *p*-*n*-junction is shown in Figure 4. Efficiency of the solar cell containing porous layer with thickness 420 nm is 35% greater than efficiency of a solar cell without of porous layer.



Figure 3 – Dependence of short-circuit current density of the solar cell on thickness of porous layer proportional to etching time

Figures 3 and 4 show that values of optimal thickness of porous layer necessary for maximum of short-circuit current $(x_{*,I})$ and solar cell efficiency $(x_{*,W})$ are equal to $x_{*,I} = 0,55$ and $x_{*,W} = 0,70$,

correspondently. These results are close to theoretical value $x_{*,W} \approx \frac{2}{3}L_D$ (is case of acceptance $L_D \approx 600$ nm according to Figure 4).





Figure 4 – Dependence of solar cell efficiency on thickness of porous *n*-layer in the direction of p-n-junction

3 Conclusions

Technology of texturing of solar cell surfaces widely used in photovoltaics in order to provide anti-reflection effects passivation and of recombination of charge carriers requires a theoretical justification. In the paper, we have theoretically shown and experimentally the existence of optimal depth of texturing in the form of porous silicon layer. Optimal values of porosity of working part of the solar cell are also described by our theory.

Results of the present work can be used for significant increasing of efficiency of solar cells (up

to 35% of the efficiency without a porous layer). Especially important that the fact of existence of an optimal set of solar cell parameters proved in the present paper can have a universal application for improvement of various technologies (electrochemical powder technology, laser surface treatment technology, technology of using organic elements, etc.).

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On the efficiency of cooled solar panels

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The photovoltaic (PV) solar panels are getting bigger applications in the practice. Their efficiency is better at lower temperatures. Normally the panels are cooled with the ambient air (in this case the gained heat is dissipated to the surrounding without any application). A successful combination of photovoltaic solar panel and solar collector is the so called photovoltaic-thermal (PV/T) solar panel. There are some significant advantages of the PV/T panels – aesthetic advantage over the PV panels, usage in places where the area is limited, reduction of the installation costs and architectural unity between roof and PV/T panels. The article analyses two solar panels – the PV solar panel of the type polycrystalline silicon (pc-Si) and the PV/T Solar Module CPVT60P250 (both solar panels are produced by the Crane Company using silicone cells from EKS – Solaris GmbH). Some tests are implemented and a comparison between the efficiencies of both panels is done.

Key words: combined photovoltaic/thermal (PV/T) solar panel, photovoltaic solar panel, natural experiments, improved panel efficiency.

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1 Introduction

Solar photovoltaic-thermal panels (or PV/T panels) are a combination of photovoltaic cells and a solar thermal collector, i.e. they are a facility that turns solar radiation into electricity and heat at the same time [1]. As a result, PV-T panels generate more energy per unit area than a combination from individual PV (photovoltaic) panels and solar thermal collectors [2]. Thus, they present a new technology where the produced heat is some times more than the electricity [3].

There are some categorizations of the PV/T panels. The first one is after the fluid used in the panel (gas or liquid). The solar PV/T air panels are not so much used in the summer time because of the limited necessity of heat [4]. The liquid PV/T panels have good applications mainly in the low-temperature range (starting by 10 to 80°C). They are used in different building installation as a coolant in evaporator circuits of "water to water" heat pumps (0 to 10 °C), in installation for heating of the pools (25 to 35 °C) and for production of domestic hot

water and heating of buildings (not more than 60 °C) [5]. On the other side the liquid PV/T panels can be divide in two different panel types depending on the upper glass cover [6]. The glass-covered PV/T panels have higher electrical efficiency compared to the glazed panels. On the other side the glazed panels possess bigger thermal efficiency than the efficiency of the glass-covered PV/T panels. There is normally done a value's combination of the average thermal and electrical efficiency.

Simultaneous optimization of electrical and thermal efficiencies was done, too. It is presented by Mohsen in [7] – an experimental study and simulation of a solar photovoltaic thermal (PV/T) air collector was implemented. The results show (Figure 1) that electrical efficiency increase with 2.5 % at relative constant thermal efficiency (for example about 51.5%). Something similar happens with the thermal efficiency – it can be higher with about 2.5% at relative constant thermal efficiency (for example about 9.3%). This concept was developed by Vilfredo Pareto and is used as effectively from the engineering designers.



Figure 1– Optimization of thermal efficiency versus electrical efficiency of PV/T collector [3]

Two thin silicon film photovoltaic panels of type ASI®-F 32/12 for 12 V applications are presented in [8-10]. Cooling pipes are mounted on the back of the first solar panel converting it in PV/ T panel. The implemented experiments with both panels are described and their characteristics have been compared. The results show that the electrical efficiency of the combined PV/ T panel is increased by about 3% compared with the standard one. Additionally – the heat output is 9 times greater than the corresponding electrical power.

The aim of the present study is to perform tests with advanced PV and PV/T modules from polycrystalline silicon (pc-Si) produced by the company CRANE [5]. The experiments will be similar to the tests implemented in [10]. The solar panels have much greater electrical power – 250Wp. The electrical parameters of both panels are identical. The construction of the PV/T panel is designed as PV module with cooling pipes added to back side at the factory [11-14]. The effect of the cooling pipes on the efficiency of the PV/T panel, and the relationships between the heat flow rate and the produced electrical power will be investigated.

2 Test installation

The modules we use are of the following types [5]:

•PV solar panel of the type polycrystalline silicon (pc-Si) photovoltaic 250 Wp;

•PV/T Solar Module CPVT60P250 with rated electrical power of 250 Wp.

Suitable applications for the above mentioned solar panels are as follows [16]:

•Grid connected systems;

•Autonomous systems.

Another suitable application for the PV/T Solar Module CPVT60P250 should be the following [17]:

•Accessing to existing heating systems for homes and office buildings, heating pool water, or cooling by means of chillers.

Here is a list of the benefits for the combined PV/T panel [17]:

•Double effect – produce electricity and heat;

•Save space 1 module for 2 systems;

•Greatly improved paybacks over the combination of traditional PV & thermal technologies;

•Provides opportunities to most residential and light commercial low energy buildings to reach zero emission;

•Increase life of solar cells;

•Suitable for off-grid installation;

•Suitable with types off installation;

•Compact design;

•Low maintenance;

•Not necessary to enter cold water to reduce hazard of preheating of the water.

The typical uses of this module include 30.5 V stand-alone applications such as lighting systems, solar home systems, displays, light and guidance systems, telecommunications, driving systems (e.g. water-pump plants, gates), robots, and mobile applications (e.g. campers). Through the connection of higher system voltages, the modules are also

excellently suited for the implementation of grid connected photovoltaic systems [18].

Some of the electrical data of both PV solar panel is shown in Table 1.

The thermal data of the Solar Module for 30.5 V-Applications CPVT60P250 is shown in Table 2.

The main components of the installation are a combined PV/T solar panel and an ordinary photovoltaic solar panel (their pictures are shown in Figure 2). Some of the measurement elements are presented there, too. Both panels are oriented to the south with a slope of 40° .

Table 1 – Electrical data of the PV solar panel of the type polycrystalline silicon (pc-Si) photovoltaic 250 Wp and solar module for 30.5 V applications CPVT60P250 [19-20]

Electrical data							
Parameter	units	value					
Number of cells	-	60					
Electrical power	Wp	250 -1 +3%					
Voltage at maximum power	V	30.5					
Open circuit voltage	V	37.8					
Current at maximum	А	8.2					
Short-circuit current	А	8.75					
Efficiency	%	15.3					
Working temperature range	°C	-40 to 85					
Maximal system voltage	V	1000					
Rated diode current	А	20					

Table 2 – Thermal data of the Solar Module for 30.5 V-Applications CPVT60P250 [5]

Thermal data						
Parameter	units	value				
Aperture area	m²	1.15				
Thermal efficiency, η_0	%	55				
Nominal heat flow rate	W	890				
Volume flow rate	l/min	1.5 - 2.5				
Flow losses	mm H ₂ O	540-880				
Fluid volume	1	1.2				
Effective thermal capacity	kJ/K	13.2				



Figure 2 –View of PV polycrystalline silicon (pc- Si) photovoltaic 250 Wp and PV/ T – CPVT60P250 panels: a) front view; b) back view

A sectional view of Solar Module CPVT60P250 is presented in Figure 3. The experimental layout is shown in Figure 4.



Figure 3 – Solar Module CPVT60P250 [5]



Figure 4 – Installation setup

A circulation pump is used to transport the cooling fluid through the combined panel and the thermostatic tank (it is used to maintain a constant fluid temperature in the PV/T panel circuit). PT100 sensors and signal conditioners are used to measure the inlet and outlet fluid temperatures in pipes. The signal is sent then to a data logger and treated by means of a Laptop or personal computer. Kipp & Zonen CMP6 pyranometer is mounted in the panel plane and is used to measure the global solar radiation.

The described installation is also used to measure the electrical power gained by both panels. For this purpose DC currents and voltages produced by the panels are measured. Two resistive loads (R_T) are connected in circuit by means to dissipate a produced electrical energy. The heat flow rate is determined, too. The main goal is to compare the electrical efficiencies of the two panels. The quantity of the gained thermal energy by the PV/T panel is calculated as well.

Experimental results

The experiment was carried out during 3 days – 16, 18 and 22 of August 2016. There were done 9 tests at different mean fluid temperatures (the mean value of inlet and outlet fluid temperature), inside the range of 25 - 60 °C. Each test had duration of about 20 min. The following parameters were measured: intensity of the global solar irradiation by means of pyranometer, ambient temperature, fluid flow rate, inlet and outlet fluid temperature trough the PV/T panel, produced electrical power by PV panel and produced electrical power by PV/T panel. The produced by PV/T panel heat flow rate, the ratio of electrical power produced by PV/T and PV panels, and the ratio of produced heat flow rate to electrical power by PV/T panel were calculated. All the mentioned parameters are shown in Table 3.

Table 3 – Test results

Parameter \ Test number	Test 1	Test 2	Test 3	Test 4	Test 5	Test 6	Test 7	Test 8	Test 9
Date	22.08.16	16.08.16	22.08.16	16.08.16	16.08.16	22.08.17	16.08.17	22.08.17	22.08.17
Start time, h	14:43	12:45	12:13	13:06	13:40	13:09	14:25	13:43	14:19
Intensity of the global solar radiation at the panel plane, W/m ²	714	787	805,5	793	754	779,78	692,46	748	763
Ambient air temperature, °C	36,6	33,98	33,57	35,07	36,4	35,64	34,81	37,23	37,08
PV cell temperature, °C	61,1	65,37	62,1	63,6	65	60,6	59,47	60,5	59,78
Flow rate, l/min	2,1	1,55	2,3	2,3	2,3	2,3	2,3	2,3	2,3
Inlet fluid temperature, °C	22,97	26	31,71	33,63	37,9	41,6	44,8	51,06	60,5
Outlet fluid temperature, °C	28,55	29,98	34,61	35,4	40,1	43,25	46,01	51,6	60,1
Fluid temperature difference, °C	5,68	3,98	2,9	1,76	2,28	1,64	1,02	0,46	-0.36
Mean fluid temperature, °C	25,82	27,99	33,16	34,52	39	42,43	45,41	51,33	60,03
Produced electrical power (PV panel), W	164,55	181,66	180,4	181,7	174,5	172,44	168,88	170,2	168,9
Produced electrical power (PV/ T panel), W	166,73	183,36	182,93	184,48	175,4	174,5	167,5	168,73	164,64
Produced heat flow rate (PV/ T panel), W	557	262,02	313,6	191,34	247,4	175,15	129,7	49,6	-39,7
Ratio of produced electrical power by PV/ T panel and PV panel, %	101,32	101,49	101,4	101,53	100,52	101,19	99,18	99,14	97,48
Ratio of produced heat flow rate and electrical power by PV/T panel	3,38	1,59	1,74	1,05	1,42	1,02	0,77	0,29	-0,24

Some results from the test number 1 are presented in Figures 5 and 6. Figure 5 shows the produced electrical power by PV and PV/ T panels on 22.08.17 starting at 14:43 h. Figure 6 presents the produced electrical and heat flow rate by PV/ T panel during the same test. Some fluctuations of the produced electricity may be observed in Figure 5 due to the clouds. All values presented in Table 3 are averaged inside the measurement range, which is chosen carefully for each single test in case to overcome the transition mode (the starting part of the tests – first 19 min in Figure 5) and to calculate a steady state values. The transition mode is due to the large heat capacity of the panel that has been heated

prior to the start of the fluid circulation through it. It is obviously that the cooled PV/T panel produces more electricity than the PV panel (Figure 6) in the steady state mode (selected measurement range – about 2,8 min long in Figure 6). Additionally the temperature of the cooling fluid increases which leads to thermal energy production.

The ratio of produced heat flow rate and electrical power by PV/T panel summarized for all nine tests is presented in Figure 7. The ratio of produced electrical power by PV/T and PV panels is presented in Figure 8. Two trend lines have been fitted to experimental data and the equation polynomials are presented also in Figures 7 and 8 respectively.



Figure 5 – Produced electrical power by PV and PV/ T panels at Test 1



Figure 6 – Produced electrical power and heat flow rate by PV/T panel at Test 1



Figure 7 – Ratio of produced heat flow rate and electrical power by PV/ T panel



Figure 8 – Ratio of produced electrical power by PV/ T panel and PV panel vs. mean fluid temperature

3 Conclusions

An experimental work to measure the electrical power of two solar panels PV PV/T types is implemented. The following conclusions can be drawn on the base of the work done:

- the PV/T panel, when is more intensively cooled by means of a fluid, has higher efficiency than the other panel; this happens in the mean temperature range up to 43 °C (Figure 8 – Higher efficiency range);

- the PV panel, has higher efficiency than the PV/T panel at the mean fluid temperatures higher than 43 °C (Figure 8 – Lower efficiency range); this is due to better PV panel cooling by the ambient air in this range;

- the electrical power produced by PV/T panel is higher by 1.5% then the electrical power produced by PV panel at the mean fluid temperatures up to 35 °C;

- the production of thermal energy is relatively high (0,29-3,38 times more than the electrical power) in the whole working temperature range (from 20 till 60°C); than lower the working temperature of the panel is, so higher the gained heat flow rate becomes because of the higher heat transfer rate and lower heat losses (Table 2);

- a good stability of the produced electrical and thermal energy in a relatively large temperature interval is reported (Fig. 8);

- compared to the earlier silicon thin film panel experiments described in [4], we have about a 2times lower effect of efficiency gain on polycrystalline PV cells produced by CRANE using combined PV/T technology.

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Modeling of low-grade pulverized coal combustion

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The article is devoted to the complex research processes of heat and mass transfer occurring in the real conditions of solid fuel (coal) combustion. Development of technological processes with economic and ecological advantages are the main purpose for many researches in thermal physics and technical physics. The complex processes of heat and mass transfer in the presence of combustion are non-stationary, strongly non-isothermal with a constant change in the physical and chemical state of the environment. It greatly complicates their experimental study. In this case, studying of heat and mass transfer in high-reacting media with simulation of physical and chemical processes occur during combustion of pulverized coal is important for the solution of modern power engineering industry and ecology problems. In this regard, a comprehensive study of heat and mass transfer processes at high-temperature media observed. Investigations based on the achievements of modern physics by using numerical methods for 3D modeling. Numerical experiments are conducted to describe and study aerodynamic characteristics, heat and mass transfer processes during the burning of pulverized Kazakhstan low-grade coal. The results obtained are of great practical importance, since they allow us to develop recommendations for the improvement and design of new combustion chambers and burners, and also can be useful in optimizing the whole process of burning fossil fuels.

Key words: aerodynamic, combustion, heat exchange, numerical experiment. PACS numbers: 47.70.Pq; 82.33.Vx; 88.20.jj; 07.05.Tp; 47.50.Cd.

1 Introduction

Solid fuel combustion is a complex physical and chemical phenomenon, which occurs at high temperatures with rapid and complete oxidation of combustible matter (carbon) by atmospheric oxygen and accompanied by a large amount of heat release [1-2]. Due to the low quality of main Kazakh coal deposits their exploitation at industry has increased scientific and applied relevance. Conducting of deep research on coal combustion in the real conditions can ensure the efficient technological process at all [3-5]. Heightened interest observed in particular to the study of heat and mass transfer processes at combustion of pulverized Kazakh coal with high ash content [6-7]. As it known combustion processes take place under conditions of strong turbulence and non-isothermal flow, multiphase medium with a significant impact of nonlinear effects of thermal radiation, interfacial interaction and multistage proceeding with chemical reactions [8-9]. Such phenomena have an important role in studying of the natural phenomenon of low-grade coal

combustion. So investigations of turbulent chemically reacting media are extremely important to deepen knowledge of physical and chemical properties, for application possibilities.

In the context of depletion of natural energy resources and environmental pollution rational use of energy fuel, increasing the efficiency of energy generation and solution of environmental problems are urgent and important task to solve. Development of technological processes with economic and ecological advantages are the main purpose for many researches in this area. The complex processes of heat and mass transfer in the presence of combustion are non-stationary, strongly nonisothermal with a constant change in the physical and chemical state of the environment. It greatly complicates their experimental study. In this case, studying of heat and mass transfer in high-reacting media with simulation of physical and chemical processes occur during combustion of pulverized coal is important for the solution of modern power engineering industry and ecology problems. In this regard, a comprehensive study of heat and mass transfer processes at high-temperature media observed. Investigations based on the achievements of modern physics by using numerical methods for 3D modeling [10-15] that in turn do not need labor force also much time. Applying of computational technology allow us to describe the actual physical processes that occur during combustion of energy fuel as accurate as possible. Finally, it has been put the objective of this paper oriented on holding numerical experiments on studying heat and mass transfer processes occurring in the areas of real geometry of the combustion chamber during the burning of energy fuel. It has been established mathematical model of physical-chemical combustion process.

2 Materials and methods

Study of processes of heat and mass transfer during coal combustion is possible only based on a complete theory of combustion physics. It includes a wide range of physical and chemical effects and its formulation of a mathematical model. For the simulation of heat and mass transfer in the presence of physical and chemical processes are used the fundamental laws of conservation of mass, momentum, energy [16-19]. Heat and mass transfer processes in the presence of physical and chemical transformations - is the interaction of turbulent flows. Therefore, the chemical processes here should take into account the law of conservation of components of the reacting mixture, multiphase medium, its turbulence degree, heat generation due to the radiation of heated fluid and chemical reactions. The law of conservation of substance written in the form of the law of conservation of matter as follows:

$$\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial x_i} (\rho u_i) = q_N. \qquad (1)$$

The law of conservation of momentum and the equation of motion expressed as:

$$\frac{\partial}{\partial t} (\rho u_i) = -\frac{\partial}{\partial x_j} (\rho u_i u_j) + \frac{\partial \tau_{ij}}{\partial x_j} - \frac{\partial P}{\partial x_i} + \rho f_{i}.$$
 (2)

Law of energy conservation:

$$\frac{\partial}{\partial t}(\rho h) = -\frac{\partial}{\partial x_{i}}(\rho u_{i}h) -$$
(3)
$$\frac{\partial q_{i}^{res}}{\partial x_{i}} + \frac{\partial P}{\partial t} + u_{i}\frac{\partial P}{\partial x_{i}} + \tau_{ij}\frac{\partial u_{j}}{\partial x_{i}} + S_{h}$$

The conservation law for the components of the reaction mixture:

$$\frac{\partial}{\partial t} \left(\rho C_{\beta} \right) = -\frac{\partial}{\partial x_{i}} \left(\rho C_{\beta} u_{i} \right) + \frac{\partial j_{i}}{\partial x_{i}} + S_{\beta} .$$
(4)

For technical flames, it takes into account the transfer of matter only by diffusion. Transfer of substance due to the pressure gradient, the action of external forces (electric and magnetic fields) and thermal diffusion are small and they be neglected. Then the last equation written as follow:

$$\frac{\partial}{\partial t} \left(\rho C_{\beta} \right) = -\frac{\partial}{\partial x_{i}} \left(\rho C_{\beta} u_{i} \right) + \frac{\partial}{\partial x_{i}} \left(\frac{\mu_{\text{eff}}}{\sigma_{\beta \text{eff}}} \frac{\partial C_{\beta}}{\partial x_{i}} \right) + S_{\beta}.$$
(5)

~

In this paper for modeling of turbulence flows used the standard k- ϵ turbulence model, excluding the effect of lift or "twist" of flow, which is represented by the equation of turbulent kinetic energy transfer:

$$\frac{\partial \left(\overline{\rho k}\right)}{\partial t} = -\frac{\partial \left(\overline{\rho u_{j}} k\right)}{\partial x_{j}} + \frac{\partial}{\partial x_{j}} \left[\frac{\mu_{eff}}{\sigma_{k}} \frac{\partial k}{\partial x_{j}}\right] + P - \overline{\rho} \cdot \varepsilon \,. \tag{6}$$

And the equation of dissipation (turbulent kinetic energy conversion into internal) turbulent kinetic energy ϵ :

$$\frac{\partial(\overline{\rho}\varepsilon)}{\partial t} = -\frac{\partial(\overline{\rho}\overline{u_{j}}\varepsilon)}{\partial x_{j}} + \frac{\partial}{\partial x_{j}} \left[\frac{\mu_{eff}}{\sigma_{\varepsilon}}\frac{\partial\varepsilon}{\partial x_{j}}\right] + . \quad (7)$$
$$+ C_{\varepsilon,1} \cdot \frac{\varepsilon}{k} \cdot P - C_{\varepsilon,2} \cdot \frac{\varepsilon^{2}}{k} \cdot \overline{\rho}$$

Here the kinetic energy production:

$$\mathbf{P} = \left[\boldsymbol{\mu}_{\text{turb}} \cdot \left(\frac{\partial \overline{\mathbf{u}_{i}}}{\partial x_{j}} + \frac{\partial \overline{\mathbf{u}_{j}}}{\partial x_{i}} \right) - \frac{2}{3} \cdot \boldsymbol{\rho} \cdot \mathbf{k} \cdot \boldsymbol{\delta}_{ij} \right] \cdot \frac{\partial \overline{\mathbf{u}_{i}}}{\partial x_{j}} \quad (8)$$

And the rate of dissipation of turbulent energy:

$$\overline{\rho} \varepsilon = \overline{\mu_{turb}} \cdot \frac{\partial u'_{i}}{\partial x_{j}} \cdot \left(\frac{\partial u'_{i}}{\partial x_{j}} + \frac{\partial u'_{j}}{\partial x_{i}} \right).$$
(9)

If k and ε are known, the turbulent viscosity determined by the Prandtl-Kolmogorov relationship as: $\mu_{turb} = c_{\mu} \rho k^2 / \varepsilon$.

Empirical constants $c_{\mu} = 0.09$; $\sigma_k = 1.00$; $\sigma_{\varepsilon} = 1.30$; $C_{\varepsilon l} = 1.44$; $C_{\varepsilon 2} = 1.92$ determined experimentally. For the turbulent numbers of Prandtl and Schmidt were taken as 0.9.

A generalized equation of the transport value in a turbulent flow will then be:

$$\frac{\partial}{\partial t}(\rho\Phi) = -\frac{\partial}{\partial x_{j}}(\rho u_{j}\Phi) + \frac{\partial}{\partial x_{j}}\left[\Gamma_{\phi,\text{eff}}\frac{\partial\Phi}{\partial x_{j}}\right] + S_{\phi}. (10)$$

To avoid mistakes that can lead to a physically meaningless result, an adequate initial and boundary conditions corresponding to real physical process given. As an object of research chosen the combustion process of Kazakh coal in combustion chamber of the real energy facility (boiler BKZ-75 of Shakhtinsk TPS in Kazakhstan). All conditions taken into account of the real process of fuel combustion. For conducting numerical modeling were used control volume method [26-27], where in computational experiment the chamber has been divided into 126 496 cells.

3 Results of numerical modeling

Following shown results of three-dimensional modeling of heat and mass transfer processes during combustion of pulverized low-grade coal in real conditions of combustion chamber of boiler. Aerodynamic pattern of motion of two-phase turbulent flow of pulverized coal combustion causes the heat and mass transfer process in general [28-30]. Figure 1 shows a two-dimensional graph of the full velocity vector, determined by the relationship: $\vec{V} = \sqrt{U^2 + V^2 + W^2}$. In the direction of camera output speed of flows decreased. The peak area values with maximum speed is clearly visible, which is equal to about 20 m/s. There at 4 meters by height of chamber located the combustor burners, and fed the fuel and oxidant mixture into the camera at maximum speed. Distribution character of flow velocity in height due to the vortex transfer of reacting medium and depending on the geometrical design of the chamber at all. At the outlet of chamber, it seen that velocity has a maximum value 8.76 m/s at section X=7.0 m and an average value not exceeding the 5 m/s by height.



Figure 1 – Distribution of full velocity vector

Figure 2 shows the distribution of maximum, minimum and average values of the temperature field in the combustion chamber. There is also observed a sharp decrease in the temperature of fuel feeding zone. This is because the fuel supplied by a lower temperature. It can be seen that temperature values reach their maximum values in the area below a girdle of the burners where located torch core (approximately at 3 meters). This is because in this area the eddy currents (from installed four burners: on 2 burners on two opposite tiers) have a maximum convective transfer that increases the residence time of coal particles in here. As a result, in this area observed temperature rise to ~1370 °C. In addition, at the output of the chamber maximum value of temperature is about 900-950 °C. This clearly seen from the 3D picture placed in the right corner of the figure. In the figure also presented the point of the theoretically calculated value of the temperature of exhaust gases in the output of the chamber defined according to the normative method of thermal calculation [31] and data from the natural experiments held in real TPP of RK [32].



Figure 2 – Temperature distribution and verification with experimental data

The method of thermal calculation in power engineering is still the most reliable for finding the temperature at the outlet of the combustion chamber. It is seen that the difference between the results of numerical calculation is small and is only 4.7%. This proves that the method of 3D modeling gives good description of real processes of heat and mass transfer of fuel combustion. The verification results show the good conformity with calculated results.

Figure 3 and 4 shows the results of 3D modeling of carbon dioxide CO_2 concentration distributions. Carbon mono oxide CO reacts with oxygen completely and so formed its dioxide CO_2 . Concentrations of carbon dioxide CO_2 have their largest amount at the top areas of chamber (section Y=3.19 m). And the minimal values are observed at the region, where the burner equipment is set. From the figure 6 at the section Y=3.19 m it is seen that concentration of carbon dioxide CO_2 has the minimal value equal to 0.0089 kg/kg. In addition, in average it raised to ~ 0.13 kg/kg at the Z=12.65 m section by height and ~ 0.15 kg/kg at the outlet of the chamber (section X=7.0 m).

These concentration distributions of carbon dioxide verified with the known data as shown in Fig. 8.

Concentrations of carbon dioxide CO_2 are in a good agreement with experimental data, received from real thermal power plant equipment [32]. By comparisons of numerical experiment results held in this work with natural data from TPP, it noticed that the difference is for carbon dioxide CO_2 is 4 %. So, considering results obtained in this paper we can propose the observed method of research of combustion processes is reliable and valid sufficiently to be useful in studying of low-grade coal combustion technological processes in energy objects.



Figure 3 - 3D distribution of the carbon dioxide concentrations on sections of the chamber



Figure 4 – Verification of calculation results with experimental data [32]

4 Conclusions and perspectives

In conclusion, with computational research of combustion and modeling of heat and mass transfer processes determined velocity characteristics of turbulent flows, their turbulent kinetic energy and dissipation energy. Aerodynamic characteristics shows that intensive mixing of fuel and oxidant held in the central part of the chamber. In addition, it caused the increasing of temperature values to 1370°C in core of torch and monotonically

decreased to 922°C at the outlet. Formation of hazardous substances as carbon oxides (CO₂) are depends on their chemical interaction with oxygen. Carbon dioxide has its maximal values at the outlet of the chamber (~ 0.16 kg/kg). Obtained results of numerical experiments have great theoretical and practical importance, as it will allow improve the design of combustion chambers and burners, to optimize the process of burning of high-ash content energy coal of Kazakhstan Republic.

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Simulation of mechanical strain of metallic electron-irradiated polyimide films

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The impact of silver metallization and electron irradiation on the physical and mechanical properties of polyimide films has been studied. The metal that impregnated the structure of the polyimide substrate was 1–5 μ m. The surface coatings contained 80–97% of the relative silver mirror in the visible and infrared regions. Irradiation was performed at the ELU-6 linear accelerator with an average beam electron energy of 2 MeV, an integral current of up to 1000 μ A, a pulse repetition rate of 200 Hz, and a pulse duration of 5 μ s. The absorbed dose in the samples was 10, 20, 30, and 40 MGy. The samples were deformed at room temperature under uniaxial tension on an Instron 5982 universal testing system. A substantial growth of mechanical characteristics resulting from the film metallization, as compared to the pure film, was observed. The growth of the ultimate strength by $\Delta \sigma = 105$ MPa and the plasticity by $\Delta \epsilon = 75\%$ is connected with the characteristics of the change of structure of the metallized films and the chemical etching conditions. The electron irradiation of new phases in the form of silver oxide in the coating. The concentration of these phases increased with increasing dose, which was also the result of the violation of new phases of silver in the coating. A mathematical model agrees with the experimental data.

Key words: polyimide, composite materials, metallization, deformation, electron irradiation, modulus of elasticity, Young's modulus, mathematical model.

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1 Introduction

Preparation and study of the metallized polymeric materials [1-4] caused by their extensive use in industry [5], electronics [6, 7], as well as in production of consumer goods [8]. Main directions of new materials search lies in obtaining composite films with different thickness metallic phase distribution retaining mechanical properties [9, 10]. The most promising variants among metallized polymeric materials are polyimides [11-13] along with their high thermal stability, good dielectric properties and low coefficient of expansion [14-17].

On the one hand, crucial moment in such studies is to identify the influence of a metallized coating type, its structure and nature on mechanical properties of the polymer composite material. On the other hand it is important to obtain constitutive equations of viscoelastic media to describe a particular type of mechanical loading, that allows to predict the performance of the material in various types of loading (static, dynamic, etc.) [18-20].

Therefore, the study of viscoelastic, strength and other mechanical properties of the metallized polymeric materials, revealing the influence of the structure of the coating on their mechanical behavior, the development of their behavior forecasting methods seems now as urgent and as important task.

2 Research technique

Metallized polyimide films of the thickness d=35 mm, obtained at the Institute of Chemical Sciences NAS RK named after Bekturov, were discovered. The first stage of the process chain comprised by obtaining polyimide different thicknesses films on the basis ABimid varnish. Technological scheme involves rolling out the varnish through spinnerets to

conveyor belt cohesive layer, followed by drying at 90°C and the thermal cyclization at 180° C for 1 and 2 hours, respectively to film rolls sizes.

The second technological scheme of obtaining roll of metallized film lies in successive processing of polyimide film original in an organic solvent, an aqueous-alcoholic alkaline solution, washing, chelation by recovering metal, washing with dialysis and thermo – chemical recover of a metal at 220 °C.

The metallized polyimide films were made as a continuous (two- or one-sided) metallic layer impregnated into the structure of the polyimide substrate. The metal phase is made of a silver of thickness of 1 to 5 microns. The overall thickness was about 25-100 micrometers depending on the initial film thickness.

Metallized coatings surface contained $80 \div 97$ % of relative silver mirror in the visible and infrared regions. Their surface resistance varied in the range of $0.1 \div 10$ ohms depending on the thickness of the metal layer and metal nature. The temperature dependency took the form of $\rho s= 0.98(1+2,65 \cdot 10^{-3t})$ in the range from -25 °C up to +200 °C.

There was no sign of detachment (delamination) of the metal surface layer until the destruction of the entire polymer layer integrity at loads of at least 160 MPa (200° C).

Number of samples of 25-100 microns thick, 5 mm wide and 70 mm (working length 50 mm) length were cut from the resulting roll of metallized PI – film, which are then were divided into 5 groups for further electron irradiation of various doses. One group of samples was taken as control variant, and was not irradiated.

Irradiation of samples was performed on a linear accelerator ELU-4. The average energy of the electron beam was 2 MeV, integral current up to 1000 mA, sending pulse frequency of 200 Hz, pulses duration of 5 ms. Absorbed dose (D) of each group of samples was respectively 10, 20, 30 and 40 MGy.

After that, the samples were deformed at room temperature in a uniaxial stretching mode using universal testing machine Instron 5982. The mechanical tests methodology was based on the use of universal testing machine Instron 5982 and Bluehill 3 software, which is designed to determine the mechanical characteristics of various materials. In Bluehill 3 test method selection is the basis of the experiment, which is assigned to the desired type of static testing. Testing was based on the GOST 25.604-82 and American standard ACTM D3039 / D 3039M – 00.

Technical characteristics of the electromechanical machine Instron 5982: maximum load of 100 kN, load measurement accuracy and deformation of ± -0.5 % of measured value.

The study of the structural changes of produced composite materials as a result of the effects of physical factors mentioned above were produced in the X-ray difraktrometre of DRON-2M type in air at a temperature of 293 K, CuK α radiation ($\lambda\alpha$ Cu=1.5418 *A*) when the counter speed 2 deg/min and feed 2400 mm/h.

3 Experimental results and discussion

Figure 1 shows the resulting relative elongation ε depending on the applied stress σ for non-irradiated metallized polyimide film.

It is seen that the metallization of polyimide film increases its elongation by 120% and breaking stress up to ~ 175 MPa. This is due to the method of preparation of these films – the chemical etching of the metal (silver in our case). The surface layer morphology of metallized samples is nanostructured, but non-uniform in terms of the volume. It appeared as 50 nm metal-packed grains. The surface layer grains have a size of 8 - 10 nm. There is a special gradient distribution of the metal in the film volume with a maximum concentration of metal on the outer layer, decreasing in accordance to depth.

Behavior of the material under mechanical deformation can be described by the following analytical expression showing dependency of ε on σ :

$$\varepsilon = \exp\left(\frac{\sigma}{E}\right)^{-1} \tag{1}$$

Expanding expression (1) into series we find that:

$$\varepsilon = \frac{\sigma}{E} + \frac{\sigma^2}{2!E} + \frac{\sigma^3}{3!E} + \dots, \qquad (2)$$

where E is the average elasticity modulus of the composite material.

The first and second terms of the series (2) describe the behavior of the material in the elastic region. The first term describes the expansion behavior of the material during the deformation in the linear part (when $\sigma < 35$ MPa), i.e. Hooke's law, and the second term of the expansion – in a non-linear (if $\sigma \ge 35$ MPa). The third term takes into account the expansion behavior of the material in the plastic field for which the value of *En* is not a modulus of elasticity, etc.

In accordance to (2) we considered the dependence $\varepsilon = f(\sigma)$ on unexposed metallized polyimide films in the elastic region, for which on the basis of experimental data the average elastic modulus of 31.7 MPa was determined. As can be seen in Figure 1, the experimental and theoretical curves matches very well until the area of loads ~ 140 MPa. The further increase in load leads to an increase of plastic deformation of the composite material, which causes it to tear, and this process requires to consider the expansion of $\varepsilon = f(\sigma)$ with subsequent members and parameters E_n .



1- experiment; 2 - calsculations

Figure 1 – Change of the relative elongation ε from applied stress σ on nonirradiated metallized polyimide films

Figure 2 (a, b) shows obtained dependencies of the relative elongation from the stress for irradiated metallized polyimide films.

Electron irradiation of the metallized film degrades its strength and elastic characteristics and elastic modulus is reduced depending on the dose of irradiation and is:

given D = 10 MGy
$$- E = 31.1$$
 MPa;
D = 20 MGy $- E = 31$ MPa;
D = 30 MGy $- E = 30.1$ MPa;
D = 40 MGy $- E = 27$ MPa.

The impact of electron irradiation on the metallized polyimide films caused the following: in process of increase of the radiation dose maximum burst relative elongation decreases. Thereby, for a dose of 10 MGy it is about 100% and for 40 MGy,

about 18%; respectively, the material strength is decreased from 160 to 80 MPa (Figure 2 a, b).

The proposed mathematical model describes the dependence of the elastic region of the relative elongation from stress of the metallized film based on polyimide as well as irradiated by electrons (see. Figure 2 a, b).

The study of the complex effects of temperature, static load (80% of the rupture) and electron irradiation on these materials showed that for nonirradiated films rupture relative elongation is ~ 90%, and the time from the beginning of the application of the load rupture – 24 minutes. For films irradiated with dose of 40 MGy – ε = 30% µ τ = 8 min., i.e. time of the load exposure on the material decreases threefold.

The electrical properties of the metallized film are also greatly impacted by a technology of production of polyimide, which leads, in particular, to a difference in surface structures on different sides of the film (glossy and matte). And it was established that the glossy side, among other things, has better optical properties than the matte, and matte has a smaller electrical resistivity.

The obtained radiographs show the changes in the structure of the material affected by electron irradiation and the effects of uniaxial mechanical stress (Fig. 3). It is evident that as a result of stretching and rupture of the unexposed film the intensity of the first peak (at about ~ 16°) decreases by about 78 units offsetting in the direction of increasing by about ~ 6° and a similar effect on the irradiated film a dose of 40 MGy causes an additional decrease in the intensity of the maximum of 20 units same offset.

The first maximum of the curve 1 indicates that the initial material had a well ordered structure. Reducing of the intensity and shift of a peak towards increasing angles after the above mentioned influences on metallized film indicates that ordering structure is disturbed and ruptures of macromolecules of the polyimide occur. These changes of the peak lead to the the fact that as a result of Compton scattering on the new centers X-ray spectrum is shifted to larger angles (θ >70°).

Occurrence and amplification of additional peaks at $\theta = 25^{\circ}$ and $\theta = 37^{\circ}$ indicates that as the result of these effects new phases with dielectric properties in the form of silver oxide are formed in the material. Amplification of these peaks is associated with the fact that electron irradiation of the metallized film causes growth of the new phase, which increases with irradiation dose.



1 - Experiment; 2 - CalculationsD = 10 MGy (a); 40 MGy (b)





3 - ruptured irradiated metallized film (D = 40MGy)

Figure 3 – Radiographs of composite materials based on a polymer

3 Conclusions

It has been established that the metallization of the polyimide film increases the the relative elongation by up to 120%, applied voltage reaches \sim 175 MPa, which is associated with the peculiarities of the structure of these films and the conditions of chemical etching.

Increasing the dose of the electron irradiation results in a decrease in rupturing elongation and, respectively, to the reduction of material strength.

The degree of metallization of the film greatly affects the growth the electrical resistivity. Increasing the radiation dose for all types of of metallization samples leads to a significant increase in the surface electrical resistance of the film. However, films with low metallization will reach saturation of conductivity with increasing irradiation dose quicker, than films with a higher degree of metallization.

Electronic irradiation and uniaxial mechanical tension of metallized polyimide film disturbs the ordered structure of the material, in the form of breaking the links of macromolecules and the formation of new phases.

Proposed mathematical model describes the behavior of the metallized polyimide films in the elastic region under the influence of uniaxial mechanical loading on films, which were nonirradiated, as well as electron-irradiated with various doses.

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