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E. A. Dmitriyeva, D. M. Mukhamedshina, K. A. Mit',
I. A. Lebedev, I. I. Girina, A. I. Fedosimova, E. A. Grushevskaja

Institute of Physics and Technology, Satbayev University, Almaty, Kazakhstan.
E-mail: dmitriyeva2017@mail.ru, muk-daniya@yandex.ru,
konstantin-mit@yandex.ru, lebedev692007@yandex.kz

DOPING OF FLUORINE OF TIN DIOXIDE FILMS SYNTHESIZED BY SOL-GEL METHOD

Abstract. Optical properties, surface resistance, adsorption sensitivity to ethanol vapor and the structure of SnO_2 nanofilms synthesized by the sol-gel method are considered in the article. An increase in the adhesion of films to the surface of a glass substrate with the addition of NH_4F has been observed. Films obtained from the sol with the addition of NH_4F have a 4-5% higher transparency than the films obtained from the sol without additives. An increase in the adhesion of films, synthesized with the addition of NH_4F, to the surface of the glass substrate was observed. The presence of F^- ions in the SnO_2 matrix is shown as additional sources of free charge carriers. Films obtained both from the sol and with the addition of ammonium fluoride exhibit a nonlinear dependence of the resistance on temperature characteristic of SnO_2. The film obtained from the sol consists of globules, separately standing or grouped. The addition of ammonium fluoride to the sol leads to the formation of a dendritic structure of the films. Films obtained both from the sol without additives and with the addition of NH_4F can be used as a sensitive element in gas analyzers to determine small concentrations of ethanol vapor. An important technical result that is a decrease in the response time to 2 seconds for ethanol vapor for both films with addition of NH_4F and without additives, is obtained. However, in order to determine concentrations from 0.1 to 0.6 mg/l, films synthesized from a sol with the addition of NH_4F are more preferred.

Key words: fluorine doping, sol-gel technology, tin oxide, structure, thin films, sensitivity to ethanol.

Introduction. Sol-gel technology is used in the production of foam for firefighting [1], the creation of continuous refractory fibers [2], to produce porous materials that are used as sorbents, catalysts or catalyst carriers [3]. The conversion of sols to gels is the basis of the latest nanotechnologies for the production of ceramic ultrafiltration membranes, optical and anticorrosion coatings, photographic materials, highly dispersed abrasives and other materials with unique properties and controlled structure [4-9].

Composite systems based on tin dioxide are a promising material for the creation of film coatings for use as active layers in gas analytical equipment [10-14]. To improve the functional properties, the films are doped. The decisive influence on the energy of surface centers is made by the defectiveness of the crystal structure (the degree of deviation from stoichiometry) [15]. Doping leads not only to the introduction of the necessary element, but also to a change in the structure and morphology of the surface of the films [16].

In this paper, the main functional properties of thin films of tin dioxide obtained from finely divided sol are investigated. The effect of the addition of NH_4F on the transparency, surface resistance, structure, and adsorption sensitivity to ethanol vapor of thin SnO_2 films is considered.

Experiment. Microscope glass slides with the following dimensions were used as the substrate for the deposition of films: length - 7.6 cm, width - 2.6 cm, height - 0.1 cm. These slides were washed with a liquid detergent, then with running water, and after that they were rinsed with distilled water. They were washed in rubber gloves to avoid contamination from contact with the skin of the hands. Then glass slides were air dried.

Ethanol (96%) was chosen as the solvent for the preparation of solutions, since it wets the glass surface better than water, has a low evaporation temperature and a high dielectric constant to ensure the dissociation of precursors. Anhydrous tetrachloride of tin was used as a reagent.

The sol of tin oxide was prepared from a solution of $SnCl_4$ in ethanol. Tin acid was completely precipitated by the addition of NH_4OH. The resulting tin-acid gel was stirred at a speed of 160 rpm and heated in parallel to 100°C to remove solvents and tin-oxide-bound water. The procedure lasted 11 hours. A white powder was obtained.

The powder of tin oxide was mixed with ethanol. Tin dioxide concentration in the solution was 0.13 mol / l. The contents of the vessel were stirred at a speed of 100 rpm (revolutions per minute) without heating until the precipitate completely transferred into solution. The procedure lasted 4 hours.

The fluorinating agent-ammonium fluoride (NH_4F) was added to the sol of tin oxide. The ratio of tin ions to fluorine ions was 10/4. The NH_4F crystals in the ethanol of tin dioxide were dissolved during 2 hours of stirring at 140 rpm with 35°C heating. The resulting sols started to coagulate 30 minutes after the stop of the flask rotation. Before applying each layer, the flask was shaken until its contents became uniform and transparent.

The sols were applied to the entire surface of the glass substrate and rotated by a centrifuge rotor to a speed of 3000 rpm for 3-5 seconds. Substrates with the remaining thin layer of sol were dried using an infrared emitter at a temperature of 80°C for 2-3 minutes. Then the sample was placed in a muffle furnace and annealed at a temperature of 400°C for 15 minutes to fix the layer on the substrate. After cooling, the next layer was applied. In total, 15 layers were applied.

Results and discussion. The thickness of the films after application of 15 layers was estimated from the change in the mass of the sample. When calculating the film thickness, the following formula was used:

$$d = \frac{m_{sample} - m_{sub}}{\rho_{SnO_2} \cdot S_{sub}}, \quad (1)$$

where d is the thickness of the film, m_{samle} is the mass of the sample, m_{sub} is the mass of the glass substrate, is the density of cassiterite taken as 7,0 g/cm^3, S_{sub} is the area of the glass substrate.

The calculated thickness of the films obtained from the sol was 60±7 nm. The films synthesized from the sol with the addition of ammonium fluoride had a larger design thickness of 90±7 nm. Since the conditions for the deposition of films on the surface of the glass substrate were the same, it is possible to assume an increase in the adhesion of the film to the substrate when NH_4F is added. In the previous work [17], films synthesized from a solution of stannous tetrachloride in ethanol were considered, their calculated thickness was 250±7 nm, under equal conditions of precipitation. It can be concluded that the formation of tin acid in the form of a gel directly on the surface of the glass substrate leads to a denser film with stronger adhesion properties than films obtained from sols containing individual dispersion particles.

Optical properties. Glasses coated with a film synthesized both from sol without additives and with the addition of NH_4F are transparent, with a white tinge and uniform throughout the surface. A photograph of the samples is shown in figure 1.

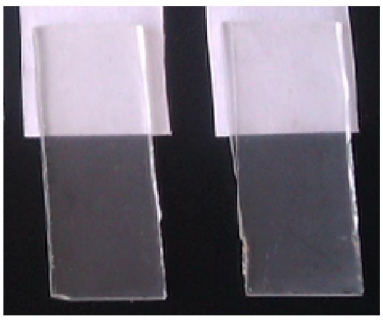

Figure 1 – Photo of samples of glasses with deposited SnO_2 films.

Left – film obtained from the sol without additives. Right – film synthesized from the sol with the addition of NH_4F

Figure 2 shows the transmission spectra of the investigated films. As can be seen from figure 2, in the visible part of the spectrum, the transparency of the films obtained from the sol varies from 58.1% at a wavelength of λ = 380 nm to 74.4% at λ =780 nm. Transparency of films synthesized from sol with the addition of NH_4F is 57.5% at λ =380 nm and 77.1% at λ =780 nm. At maximum sensitivity of the human eye to electromagnetic radiation (λ=555 nm), the films have a transparency of 70 and 71%. Transparency of films with increasing wavelength increases to 85 and 86%. Films obtained from the sol with the addition of NH_4F in the wavelength range from 550 to 2300 nm have a transparency 4-5% higher than the films obtained from the sol without additives. Optical excitation of electrons in a semiconductor thin-film structure does not have any noticeable effect on the semiconductor [18]. However, determination of the optical parameters of the layer and its thickness is possible, if the transmission spectrum demonstrates interference fringes. As the thickness of the films decreases, the interference extrema are removed from each other [19]. In our case, interference fringes on transmission spectra are not observed, which may be due to the absorption in the film or to the scattering of electromagnetic radiation from uneven surfaces.

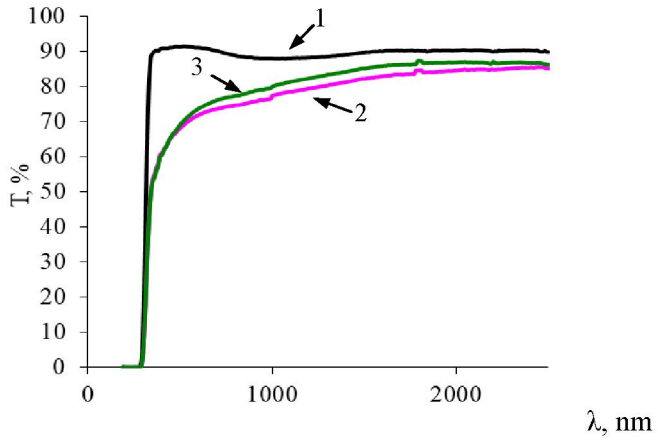

Figure 2 – Transmission spectra of tin dioxide films:
1 – glass substrate; 2 – film obtained from sol without additives; 3 – film synthesized from a sol with the addition of NH_4F

Surface resistance. The surface resistance of the films was measured at room temperature by the Van der Pauw method. The films obtained from the sol had a surface resistance of 78.9±6.9 kΩ/square. Films synthesized from the sol with the addition of ammonium fluoride had a surface resistance of 69.4±8.3 kΩ/square. The decrease in the surface resistance confirms the inclusion of F^- ions in the SnO_2 matrix [20] as additional sources of free charge carriers. The high resistance of the samples can be due to the small calculated film thickness. Belousov et al. [21] noted an increase in the resistance of films synthesized from solutions after gelling.

The dependence of film resistance on temperature, which is used in thin-film thermistors, is of practical importance. Figure 3 shows the temperature dependence of the resistance of the investigated films. It can be seen that the films obtained both from the sol and with the addition of ammonium fluoride exhibit a nonlinear dependence of the resistance on temperature, which is characteristic of SnO_2. When heated, the kinetic energy of the valence electrons rises, a disruption of individual bonds occurs, and the number of electrons that are released increases, and the resistance decreases (the initial part of curves 1.2 in figure 3).

At a temperature of 120°C, adsorption and chemisorption of oxygen from the air by the oxygen vacancies of the SnO_2 film begin to predominate. The formation of chemisorbed oxygen molecules (O_2^-, O^-, O^{2-}) requires the transition of electrons from the conduction band to the surface states, which leads to a decrease in the concentration of free charge carriers, and so the decrease in resistance stops (a flat section on curves 1 and 2 in figure 3).With a further increase in temperature from 260°C and higher, the scattering of free charge carriers on structural defects is affected, and the resistance begins to grow.

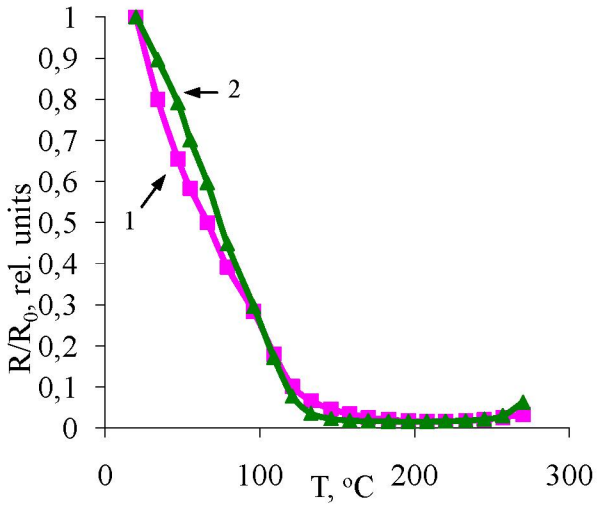

Figure 3 – Dependence of resistance on temperature:
1 – film obtained from sol without additives; 2 – film synthesized from a sol with the addition of NH_4F

Structure of the films. Figure 4 shows the surface images of the investigated films. It can be seen that the film obtained from the sol consists of globules separately standing or grouped. The size of separately standing globules is of the order of 5μm. It can be assumed that this type corresponds to the dispersed phase of SnO_2 obtained in solution. The presence of free space between globules can cause high resistance of the films, as well as it can be a source of light scattering. The addition of NH_4F led to the formation of the dendritic structure of the films. Separate globules are not observed. The free space between the structures reaches 10-15μm. The resulting structures do not exclude the presence in the film of many chaotically oriented crystallites of SnO_2.

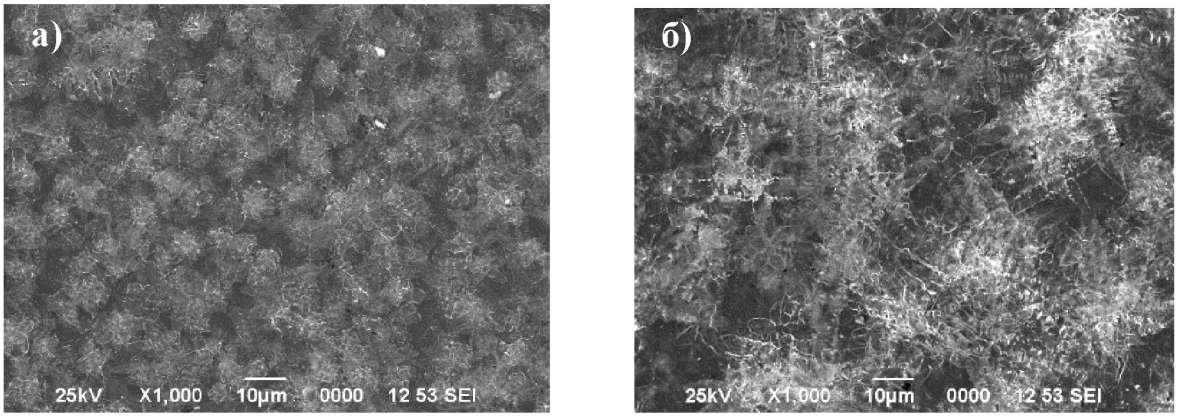

Figure 4 – Surface topography of SnO_2 films:
a – film obtained from sol without additives; b – film synthesized from sol with the addition of NH_4F

Sensitivity to ethanol vapor. The sensitivity to ethanol vapor was determined as the ratio of film resistance in pure air to the film resistance in the presence of ethanol vapor of a certain concentration and it was carried out in two stages. At the first stage, the sample temperature T_s was set, at which the maximum sensitivity of the film under study to ethanol vapor was achieved. At the second stage, at the temperature found, the change in film resistance was measured under the action of various concentrations C_{eth} of ethanol vapor.

Figure 5a shows the temperature dependence of the sensitivity of thin SnO_2 films to ethanol vapor at a concentration of 1mg/l. Films obtained from sol without additives begin to exhibit sensitivity (R_0/R =1.02) at a temperature of 160°C.

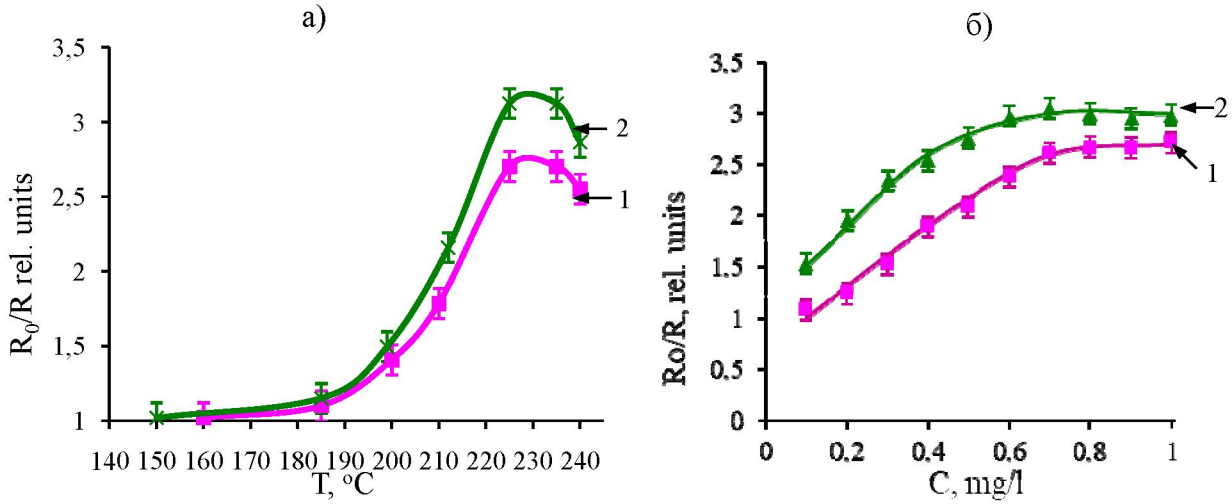

Figure 5 – Sensitivity of thin SnO_2 films to ethanol vapor:
1 – film obtained from sol without additives; 2 – film synthesized with the addition of NH_4F;
a) on different sample temperatures at the ethanol concentration of C_{eth}=1mg/l;
b) on different concentrations of ethanol at the sample temperature of T_s=230°C

Fluorine doping led to a decrease in the temperature, at which a change in the resistance of the films was detected in the presence of ethanol vapor, and it was 150°C. At this temperature, the horizontal section of the curves of the film resistance versus temperature begins (figure 3). This indicates the reaction of chemisorbed oxygen molecules on the surface of films with ethanol molecules. Further increase in substrate temperature leads to an increase in sensitivity. The maximum sensitivity was observed at a substrate temperature of 230°C.

An increase in substrate temperature above 230°C leads to a decrease in sensitivity. The sensitivity of films synthesized from the sol of tin oxide without additives was 2.7±0.1 rel. units at a temperature of 230°C. For films with the addition of ammonium fluoride, it was 3.0±0.1 rel. units. The increase in film sensitivity may be due to an increase in the amount of SnO_2 particles on the surface of which adsorption-desorption reactions occur, due to an increase in the contact between individual sol particles and the formation of a dendritic structure.

Figure 5b shows the sensitivity versus the concentration of ethanol vapor. It can be seen that films obtained from sol without additives do not have sensitivity to ethanol vapor of 0.1mg/l, and films doped with fluorine have a sensitivity of 1.5 rel. units. An increase in the concentration of ethanol vapor leads to an increase in sensitivity. When ethanol vapors of concentrations of 0.6-0.7mg/l and above are used, the sensitivity of the films varies within the limits of measurement accuracy.

The effect of the same change in the film resistance for various gas concentrations is related to the "saturation" of the active centers on which adsorption-desorption reactions occur. That is, all the centers of chemisorbed oxygen, which are on the surface of the film, are already involved in the interaction with ethanol, and so a further increase in the concentration of ethanol does not lead to an increase in the released electrons.

Thus, films obtained both from the sol without additives and with the addition of NH_4F can be used as a sensitive element in gas analyzers to determine small concentrations of ethanol vapor. However, in order to determine concentrations from 0.1 to 0.6 mg/l, films synthesized from a sol with the addition of NH_4F are more preferred.

One of the important parameters for the gas analyzer equipment is the response time of the sensor. Serially produced breathalyzers (in particular: Pft-838 digital, Breathalyzer at65s, Breathalyzer 2017, Professional Breath Alcohol Tester, Pft-642s 2017 popular mini) have a response time of about 5 seconds. The response time is 90% of the time for which the film resistance reaches a minimum value when ethanol vapor is released. Films obtained both from the sol without additives and with the addition of NH_4F have a response time to ethanol vapor absorption of 1mg/l in concentration of less than 2 seconds. Thus, an important technical result is obtained, that is a decrease in the response time to 2 sec.

Conclusion. An increase in the adhesion of films to the surface of a glass substrate on the addition of NH_4F into sol has been observed. Films obtained from the sol with the addition of NH_4F are 4-5% more transparent than the films obtained from the sol without additives. The presence of F^- ions in the SnO_2 matrix is shown as additional sources of free charge carriers. The film obtained from the sol consists of globules, separately standing or grouped. The addition of NH_4F led to the formation of the dendritic structure of the films.

The technical result is consisted in decreasing the response time to 2 seconds to ethanol vapor for films obtained both from the sol without additives and with the addition of NH_4F. Films obtained from sol with the addition of NH_4F are more preferable for use as a sensitive element in gas analyzers, for determination of ethanol vapors from 0.1 to 0.6 mg/l.

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Е. А. Дмитриева, Д. М. Мухамедшина, К. А. Мить, И. А. Лебедев, И. И. Гирина, А. И. Федосимова, Е. А. Грушевская

Физика-техникалық институты, Сәтбаев университеті, Алматы, Қазақстан

ЗОЛЬ-ГЕЛЬ ӘДІСІМЕН СИНТЕЗДЕЛГЕН ҚАЛАЙЫ ДИОКСИДІ ҚАБЫРШАҒЫН ФТОРМЕН ЛЕГІРЛЕУ

Аннотация. Мақалада золь-гель әдісімен синтезделген SnO_2 наноқабыршақтың және этанолдың буының адсорбциялық сезгіштігі, үстіңгі қабатының кедергісі және оптикалық қасиеттері қарастырылды. Шыны төсеніштің бетіне NH_4F қоспасымен қосу барысында, қабыршақтың адгезиясының ұлғаюы анықталды. NH_4F қоспасымен алынған қабыршақтар, қоспасыз алынған қабыршақтардан 4-5% жоғарғы мөлдірлі қасиеті бар. SnO_2 матрицасындағы F^- иондарының болуы, еркін заряд тасымалдаушыларының қосымша көзі ретінде көрсетілді. Зольмен алынған және аммоний фторидының қоспасынан алынған SnO_2 қабыршағы, температура бойынша кедергінің сызықты емес тәуелділігі сипаттамасын көрсетеді. Зольмен алынған қабыршақ, жекеленген немесе топтастырылған глобулдан тұрады. Зольмен қоспасыз және NH_4F қоспасымен алынған қабыршақтарды, этанол буының шағын концентрациясын анықтау үшін, газды анализаторда сезгішті элемент ретінде қолдануға болады. NH_4F қоспасымен және қоспасынсыз алынатын қабыршақтары үшін,этанол буының кему уақытының әсері 2 секунд болатын, маңызды техникалық нәтижесі алынды. Алайда, 0,1–0,6 мг/л аралығындағы концентрацияны анықтау үшін, зольмен және NH_4F қоспасымен алынған қабыршақтары қолайлы болып келеді.

Түйін сөздер: фтормен легірлеу, золь-гель технологиясы, қалайы оксиді, жұқа қабыршақтар, этанолға сезгіштігі.

Е. А. Дмитриева, Д. М. Мухамедшина, К. А. Мить, И. А. Лебедев, И. И. Гирина, А. И. Федосимова, Е. А. Грушевская

Физико-технический институт, Сатпаев университет, Алматы, Казахстан

ЛЕГИРОВАНИЕ ФТОРОМ ПЛЕНОК ДИОКСИДА ОЛОВА СИНТЕЗИРОВАННЫХ ЗОЛЬ-ГЕЛЬ МЕТОДОМ

Аннотация. В статье рассмотрены оптические свойства, поверхностное сопротивление, адсорбционная чувствительность к парам этанола и структура нанопленок SnO_2, синтезированных золь-гель методом. Пленки, полученные из золя с добавлением NH_4F, имеют на 4-5% более высокую прозрачность, чем пленки, полученные из золя без добавок. Обнаружено увеличение адгезии пленок, синтезированных с добавлением NH_4F, к поверхности стеклянной подложки. Показано наличие ионов F^- в матрице SnO_2 в качестве дополнительных источников свободных носителей заряда. Пленки, полученные как из золя, так и с добавлением фторида аммония демонстрируют характерную для SnO_2 нелинейную зависимость сопротивления от температуры. Пленка, полученная из золя, состоит из глобул, отдельно стоящих или сгруппированных. Добавление фторида аммония к золю привело к образованию дендритной структуры пленок. Пленки, полученные как из золя без добавок, так и с добавлением NH_4F, могут быть использованы в качестве чувствительного элемента в газоанализаторах, для определения малых концентраций паров этанола. Получен важный технический результат – уменьшение времени отклика до 2 секунд к парам этанола как для пленок с добавлением NH_4F, так и без добавок. Однако, для определения концентраций от 0,1 до 0,6 мг/л более предпочтительны пленки, синтезированные из золя с добавлением NH_4F.

Ключевые слова: легирование фтором, золь-гель технология, оксид олова, структура, тонкие пленки, чувствительность к этанолу.

Information about authors:

Dmitriyeva E. A., Institute of Physics and Technology, Satbayev University, Almaty, Kazakhstan; dmitriyeva2017@mail.ru; https://orcid.org/0000-0002-1280-2559

Mukhamedshina D. M., Institute of Physics and Technology, Satbayev University, Almaty, Kazakhstan; mukdaniya@yandex.ru; https://orcid.org/0000-0003-2513-6855

Mit' K. A., Institute of Physics and Technology, Satbayev University, Almaty, Kazakhstan; konstantinmit@yandex.ru; https://orcid.org/0000-0002-0078-6723

Lebedev I.A., Institute of Physics and Technology, Satbayev University, Almaty, Kazakhstan; lebedev692007@yandex.kz; https://orcid.org/0000-0002-7562-9925

Girina I.I., Institute of Physics and Technology, Satbayev University, Almaty, Kazakhstan; https://orcid.org/0000-0002-4706-5261

Fedosimova A.I., Institute of Physics and Technology, Satbayev University, Almaty, Kazakhstan; https://orcid.org/0000-0001-9607-6074

Grushevskaja E.A., Institute of Physics and Technology, Satbayev University, Almaty, Kazakhstan; https://orcid.org/0000-0001-6745-5462

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