УДК 539.23: 621.793

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INFLUENCE OF PLASMA TREATMENTS ON PROPERTIES OF THE SnO_2 AND ZnO THIN FILMS PREPARED BY THE SOL-GEL TECHNIQUE

Abstract. SnO_2 and ZnO thin films were synthesized by sol-gel technique. Then films were treated by glow discharge O- and H-plasmas. The structure, optical and morphological characteristics of films were measured and analyzed. The correlations between crystallite sizes and the morphological characteristics of films have been extracted on the basis of the frontier computational analysis of the scanning probe microscope (SPM) data matrices. Measurements of X-ray diffraction and optical transmittance spectra have confirmed the computational results. The discovery size-morphology correlations in thin oxide films might open new avenues ultimately leading towards deeper insight into unsolved problems of evaluation of optimal technological conditions for thin oxide film designing.

Keywords: oxygen or hydrogen plasma, sol-gel technique, tin oxide, zinc oxide.

Тірек сөздер: оттегі және сутегі плазмасы, sol-gel әдісі, мырыш тотығы, қалайы тотығы.

Ключевые слова: кислородная или водородная плазма, золь-гель технология, оксид олова, оксид цинка.

INTRODUCTION. Metal oxide nanostructures have attracted great interest due the large variety of physical properties they present. The importance of transparent conducting oxides (TCO) in the field of future production of electric energy by sun light conversation has become unquestionable over the past time, as using TCO for front contact or intermediate reflector are one of the technological key points of solar cell designing [1-4]. Formation condition of metal oxides films significantly influences on the structure, surface morphology and their electrophysical properties. Among the various perspective physiccal and chemical methods of thin films deposition sol-gel process has distinct advantages over other techniques due to excellent composition control, homogeneity on the molecular level, simplicity of impurity doping process, high porosity and small crystallite sizes of synthesized films [5]. Recently, the plasma treatments have been widely used for modification of semiconductor metal oxide thin films [6-8].

This article presents the effects of hydrogen and oxygen glow discharge plasma on the structure, morphology and optical properties of SnO_2 and ZnO thin films prepared by the sol-gel technique.

EXPERIMENTAL

SnO_2 and ZnO thin films were obtained by a sol-gel technique. The films were deposited on cleaned microscopy glass slides. A colloidal solution was preparing by dissolving of anhydrous stannic chloride ($SnCl_4$) in ethanol for making the films of tin dioxide. Zinc acetate dehydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$) had been dissolved in an isopropanol (C_3H_7OH) with addition of hydroxide ammonium (NH_4OH) for deposition of zinc oxide films. The films were deposited on cleaned microscopy glass slides by spin coating at 3800 rpm (revolutions per minute). The rotation time was 3-5 s. The films were heated up by an infrared radiation lamp up to 80°C for elimination of organic residues. Then the samples were annealed at a temperature of 400°C for 15 min. There were 15-deposited layers for SnO_2 and 9 layers for ZnO films. The thickness of the deposited film was estimated from the weight of the film and was about 300 nm.

The glow discharge oxygen or hydrogen plasma was generated at the pressure of 6.5 Pa with a capacitive coupled radio frequency (r.f. 27.12 MHz) power of about 12.5 W. The temperature of processing did not exceed 100°C. The processing time was 5 min.

The film's structure was investigated by X-ray diffraction using a narrow collimated (0.05x1.5 mm^2) monochromatic (CuK_α) X-ray beam directed at an angle of 5° to the sample surface. The intensity of X-ray radiation along the diffraction patterns was measured by $2\theta = 0.05°$ steps. The average crystallite size estimated from the width of X-rays lines by Jones method. The optical transmittance spectra had been measured in the wavelength range from 190 nm to 1100 nm by means of the SF-256 UVI and from 1100 nm to 2500 nm by means of the SF-256 NIR spectrophotometers (LOMO, Russia). The surface morphology was investigated using atomic force microscope (JSPM 5200 Jeol, Japan). Scanning of the surface was carried out in air at the room temperature.

RESULTS AND DISCUSSION

Optical properties of SnO_2 and ZnO thin films

The optical transmittance spectra of synthesized SnO_2 and ZnO thin films before and after treatments by glow discharge hydrogen and oxygen plasmas are shown in Fig.1a and b, respectively. Plasma processing of SnO_2 films weakly influences on their transmission spectra in the wavelength range from 300 to 1200 nm (Fig. 1a).

Fig.1b shows the optical transmittance spectra of the thin ZnO films for as-synthesized and treated by the glow discharge oxygen (Fig. 1b, curve 3) or hydrogen plasma (Fig. 1b, curve 4). The optical transmittance spectra have shown that all films exhibit high transmittance in the 350-600 nm range (about 80%). Transmission, however, falls very sharply in the UV region due to the onset of fundamental absorption.

The appreciable decreasing of optical transmittance $T(\lambda)$ after processing of ZnO film by the oxygen plasma (Fig. 1b, curve 3) is taken place on wavelengths more than 1000 nm. After treatment by hydrogen plasma (Fig. 1b, curve 4) the transparency of a film slightly decreased in the region of small wavelengths.

The optical transmittance in the visible range was about 90%. Optical constants for all tin oxide films were estimated by the envelope method from the transmittance data. The optical band gap was determined from the allowed direct transition. The porosity and density are determined using the equation of Lorentz-Lorenz [9]. The obtained results are shown in Table 1.

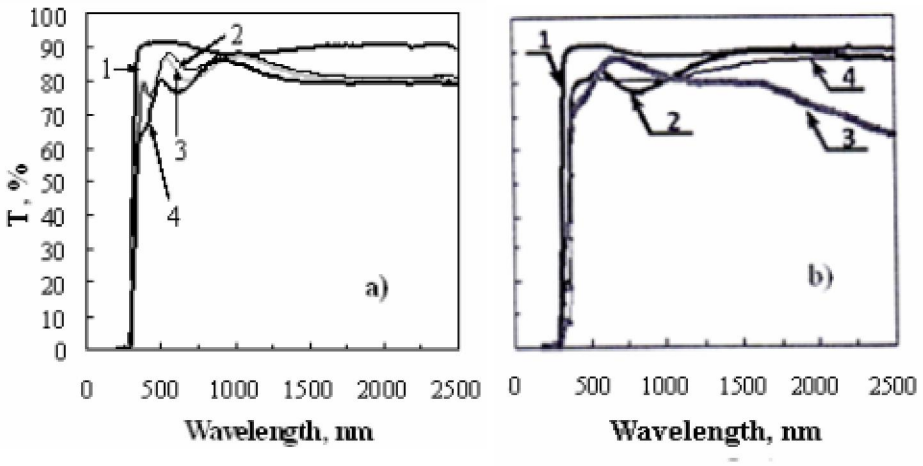

Figure 1 – Optical transmittance of SnO_2 (a) and ZnO (b) thin films on glass substrate. SnO_2 (a): glass substrate (1), as-synthesized (2), treated by O-plasma (3) and H-plasma (4); ZnO (b): glass substrate (1), as-synthesized (2), treated by O-plasma (3) and H-plasma (4)

Table 1 – Calculated optical parameters of SnO_2 films

Samples	Refractive index, n	Thickness, nm	Optical band gap, E_g, eV	Absorption coefficient, k, cm^{-3}	Porosity V, %	Density ρ, g/cm^3
SnO_2	1.741	316	4.10	$2.50 \cdot 10^3$	22.3	5.40
O-plasma	1.816	297	4.10	$3.05 \cdot 10^3$	16.5	5.80
H-plasma	1.734	288	4.00	$5.91 \cdot 10^3$	22.8	5.36

The band gap energy of ZnO determined from the assumption of direct transitions, increases at processing by hydrogen plasma and is reduced at processing by oxygen plasma. The as-deposited, oxygen plasma treated and hydrogen plasma treated ZnO samples have optical band-gap energy of 3.42 eV, 3.37 eV and 3.6 eV, respectively. The increase band-gap energy after hydrogen plasma treatment probably specifies occurrence of the shallow hydrogen donors. The reduction of band-gap energy after oxygen plasma processing can occur due to reduction of ZnO grain sizes and changes in the nature of bond potentials between internal defects and the basic material [10].

Structure properties of SnO_2 and ZnO films

Fig. 2a,b,c shows XRD patterns of SnO_2 thin films annealed at 400°C for 15 min and after treatments by glow discharge hydrogen and oxygen plasmas, respectively. The structure of SnO_2 crystal grains was sufficiently good formed. It takes place providing registration of X-ray reflections from 7 planes with Miller indices (110), (101), (200), (211), (220), (112), (301).

As it has been shown earlier [6, 11] the growth of absorption in the near IR range after plasma treatment can occur as a result of the increase of free charge carrier concentration due to the presence of subnanometer Sn clusters or Sn crystallites. Plasma processing weakly influences on absorption in the near IR range of SnO_2 films synthesized by sol-gel technique. It indicates the absence of tin nanoparticles in these films due to their better stoichiometry.

This assertion is confirmed by the X-ray data of the average sizes of crystallites of SnO_2 films (Table 2). The treatment in the oxygen plasma leads to a reduction of the average crystallites sizes. The reduction can be caused by crystallization of amorphous fraction and formation of SnO_2 crystallites with small sizes. This assumption is confirmed by visible increase of amplitudes and integral intensity of SnO_2 peaks. In contrast, processing by hydrogen plasma causes the growth of average crystallite sizes demonstrating its segregating influence.

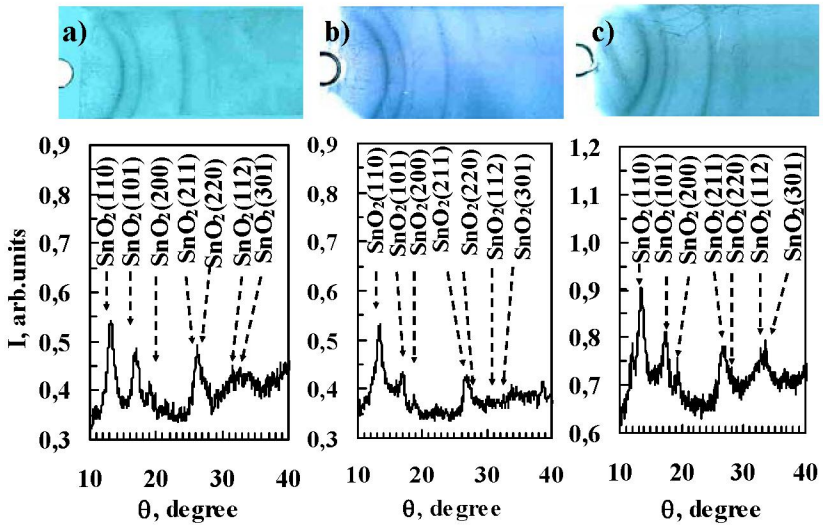

Figure 2 – X-ray diffraction pattern and X-ray intensity curves for thin SnO_2 films on the glass substrate after deposition (a), after treatment during 5 min by glow discharge oxygen (b) and H-plasma (c)

Table 2 – Average size of crystallites (nm) for the SnO_2 and ZnO films estimated from XRD-patterns

Samples	SnO_2(101)	SnO_2(200)	SnO_2(211)	SnO_2(110)	ZnO(100)	ZnO(002)	ZnO(101)
as-deposited	6.5	6	6	5	15	14	13
O-plasma	6	5.5	4.5	5.5	14	12	12
H-plasma	9.5	10	10	6.5	19	–	16

Fig. 3a,b,c shows XRD patterns of ZnO thin films synthesized and after treatments by glow discharge hydrogen and oxygen plasmas, respectively. XRD patterns show that in the zinc oxide film only ZnO polycrystalline phase was observed, 7 lines typical for ZnO were revealed (Fig. 3a). The hydrogen plasma treatment results (Fig.3b) in partial destruction of crystallites structure and disappearance of X-ray lines with Miller indices (102), (002), (110), (103), (112). It could be associated with destroying influence of hydrogen plasma streams on structural perfection of zinc oxide crystallites. As shown in [11], hydrogen forms in ZnO crystals the donor centers which concentration strongly grows after processing in hydrogen plasma; however, such treatment does not lead to effective passivation of deep traps. Processing in oxygen plasma results a reduction of the crystallites sizes, but the quantity of X-ray lines is not changed (Table 2).

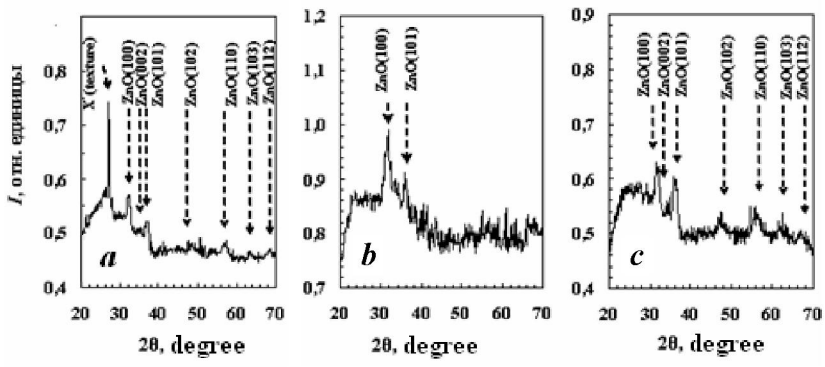

Figure 3 – X-ray intensity curves for thin ZnO films on the glass substrate after deposition (a), after treatment during 5 min by glow discharge oxygen (b) and H-plasma (c)

The amplitude and integrated intensity of ZnO peaks are increased for both plasma treatments. Growth of integrated intensity of peaks could be caused by oxidation of the excess zinc atoms in as-deposited film. Really, observable reduction of a transparency in NIR range of the transmittance spectra at processing by

oxygen plasma (Fig. 1b, curve 3) is occurred, probably, due to formation of fine metal nanoparticles which size could be insufficient for formation of Zn crystallites, but sufficient for growth of IR absorption. It is possible only in case of presence of superfluous zinc atoms in the film, which under influence of oxygen is transformed into ZnO, and nanoclusters of Zn. A similar decrease of the transparency in the NIR range was observed in [6] after short-term treatment by oxygen plasma of SnO_x layers synthesized by magnetron sputtering containing excess tin atoms.

Atomic force microscopic study of SnO_2 and ZnO films

The topography of the SnO_2 and ZnO surface films both before and after plasma treatments has been investigated by AFM. The AFM images (500?500 nm) are presented in Fig. 4. The as-synthesized films (Fig. 4a, d) have fine-grained structure with a wide spread of the particles sizes. The surface structure of ZnO film is more granular in comparison with the same of SnO_2 film. Since the sizes of ZnO grains are large and lie between 20-100 nm, it is likely that the grain consist of crystallites.

As it was mentioned above (paragraph 3.2), processing by hydrogen plasma causes the growth of average crystallite sizes demonstrating its segregating influence. It is also seen (Fig. 4c, f) that the formation of large grains occurred during processing by hydrogen plasma. Destroying influence of hydrogen plasma streams on structural perfection of zinc oxide crystallites and disappearance of X-ray lines with Miller indices (102), (002), (110), (103), (112) was shown in Fig.3. As is also seen on Fig. 4f, the grain boundaries become less clear and more blurred.

As it was stated earlier (paragraph 3.2) the treatment by oxygen plasma leads to a reduction of the average crystallites sizes. As is seen on Fig.4b and e, the treatment by oxygen plasma results in destruction of granular structure of film. One can assume clustering of the surface during processing by oxygen plasma.

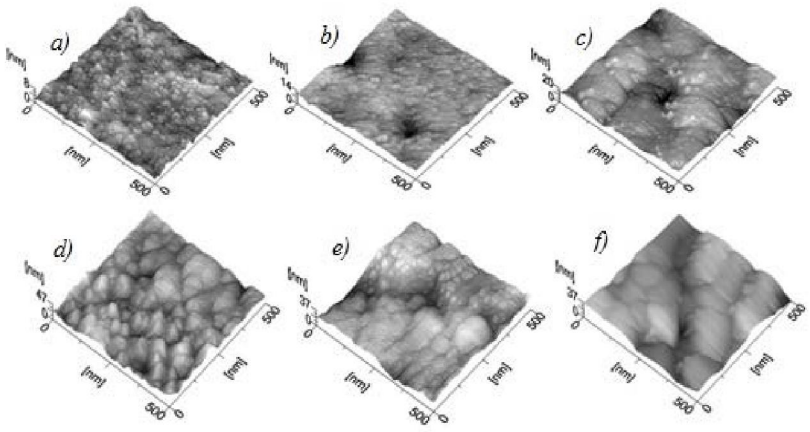

Figure 4 − 500?500 nm AFM AC images of the SnO_2 and ZnO films microstructure:
(a) – SnO_2 as-synthesized; (b) − SnO_2 treated by O-plasma; (c) − SnO_2 treated by H-plasma,
(d) – ZnO as-synthesized; (e) − ZnO treated by O-plasma; (f) − ZnO treated by H-plasma

In Table 3 the results of image analysis of SnO_2 and ZnO films surfaces using the AFM software are shown. The roughness is increased after processing of SnO_2 films by both hydrogen and oxygen plasma, especially after hydrogen plasma treatment due to the formation of granular structure of film surface (Fig.4c). The roughness of ZnO film is decreased after processing by oxygen plasma due to the intensive destructive influence of oxygen plasma processing on well-formed granular structure of as-deposited ZnO film. As one can see from the Table 3 and Fig.4, the roughness of ZnO films exceeds the same of SnO_2 films both before and after plasma treatment, because the structure of ZnO film is more granular in comparison with the same of SnO_2 film. The as-synthesized films have fine-grained structure with a wide scatter of the sizes of particles. Treatment by oxygen plasma leads some destruction of granular structure of films and to a decrease of grains sizes, confirming the assumption about its cluster structure after oxygen plasma processing. In contrast, the treatment by hydrogen plasma leads the increase of grain sizes showing a segregating effect of hydrogen plasma.

Table 3 –The analysis of surface images of SnO_2 and ZnO films (500?500 nm) surface

Samples	R_s, nm	R_q	R_z, nm
Glass substrate	2.31	2.92	19.0
SnO_2 film as-synthesized	0.66	0.84	7.02
O-plasma	1.15	1.58	13.6
H-plasma	2.04	2.61	19.7
ZnO film as-synthesized	5.37	6.71	47.2
O-plasma	4.88	6.08	37.0
H-plasma	5.38	6.58	37.4
R_s – average roughness, nm; R_q – root mean square roughness; R_z – maximum difference between high and low height, nm.			

Substantial growth of a surface roughness of SnO_2 films after plasma processing leads to increase the proportion of absorbed radiation (Fig.1), the maximum scattering of the incident radiation, the optimization of light absorption.

The studies clearly shows that the analysis results of synthesis of metal oxide thin film requires research of optical, morphological and structural film's features, i.e. requires use of the different measuring platform collection and consequently substantial time and financial resources. In work [12] we have processed the data on the effect of plasma treatment for time only on the basis of measurements of the topography of the ZnO films testing. The estimation of size and morphology correlation is a way to create a nanolaboratory on the single measuring platform by means of mathematical and computing tools, which would enable to obtain a set of morphological and structural film's features. The crystallite sizes in thin films (in the limiting case – two-dimensional structures), from general point of view, should be recognized in morphological features of the surface. Detection and recognition of these very weak correlations requires precise measurement tools and effective analysis methods. The correlation estimates were obtained on the basis of effective methods of spectral and clustering analyzes. All computations were performed on the groundwork in the field of scanning probe microscopy, neural network computing and wavelet analysis in the environment of MATLAB software platform.

Size-property relations in plasma-modified ZnO thin films have been established as a function of plasma treatment duration. It has been shown that duration of plasma treatment is a key parameter of thin oxide modifications. The correlations between crystallite sizes and the morphological characteristics of films have been extracted on the basis of the wavelet and self-organizing map analyzes of the scanning probe microscope (SPM) data matrices. The nanocluster structure of oxide films have been studied in detail with accuracy corresponding to the results of the SPM with a tenfold sharper cantilever tip. The strong plasma-induced changes in crystallite sizes have been interpreted as a size-structure phase transition. Direct measurements of X-ray diffraction and optical transmittance spectra have confirmed the computational results. The exploration of size-property relations has shown that SPM and effective spectral and clustering approaches can be very useful not only at analyzes but also at optimal property designing of thin oxide films for promising nanophotonics devices.

CONCLUSIONS. The influence of treatments by glow discharge hydrogen or oxygen plasmas on optical properties, structure and morphology of SnO_2 and ZnO thin films received by sol-gel technique was studied. It is shown that plasma processing weakly influences on absorption in the near IR range of SnO_2 films synthesized by sol-gel technique indicating the absence of tin nanoparticles in these films due to their high stoichiometry. In contrast, the observable reduction of a transparency in near IR range after short-term processing of ZnO films by oxygen plasma indicates a formation of fine metal nanoparticles which size could be insufficient for formation of Zn crystallites, but sufficient for growth of IR absorption.

It was shown, that the structure of as-deposited ZnO film is more granular in comparison with the same of SnO_2 film. Since the ZnO grains are large (20-100 nm), it is likely that the grains consist of crystallites. The treatment in oxygen plasma leads to the reduction of the both crystallite and grain sizes and the processing by hydrogen plasma cause the insignificant growth of the same sizes. Growth of a roughness of a surface SnO_2 films after plasma processing leads to increasing, as against ZnO films to light absorption.

The possibility of increasing the efficiency of carrier generation in solar cells using plasma treatment TCO front contact or intermediate reflector SnO and ZnO films for better scattering of incident light and the multiple reflections of photons can be applied.

The discovery size-morphology correlations in thin oxide films might open new avenues ultimately leading towards deeper insight into unsolved problems of evaluation of optimal technological conditions for thin oxide film designing.

ACKNOWLEDGEMENT. This work was supported by grant of Ministry of Education and Science of Republic Kazakhstan. The authors are very grateful to Dmitriyeva E.A. and Gritskova E.V.for preparation of SnO_2 and ZnO films, respectively.

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Резюме

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ЗОЛЬ-ГЕЛЬ ӘДІСІМЕН СИНТЕЗДЕЛГЕН SnO_2 ЖӘНЕ ZnO ЖҰҚА ПЛЕНКАЛАРДЫҢ ҚАСИЕТІНЕ ОТТЕГІ ЖӘНЕ СУТЕГІ ПЛАЗМАСЫМЕН ӨҢДЕУДІҢ ӘСЕРІ

Жұқа SnO_2 және ZnO пленкалары золь-гель әдісімен синтезделді. Сонан соң пленкалар солғын разрядты О- және Н-плазмасымен өңделді. Құрылымы, оптикалық және морфологиялық сипаттамалары өлшенді және

талданды. Кристаллиттердің өлшемі мен морфологиялық сипаттамасының арасындағы корреляция сканирлеуші зондтық микроскоптың (СЗМ) деректерінің матрицасын компьютерлік талдаудың негізінде алынды. Рентгендік спектрлерді және оптикалық өткізудің спектрлерін өлшеу компьютерлік нәтижелерді дәлелдеді. Жұқа тотықтық пленкаларды синтездеу үшін жұқа тотықтық пленкаларда мөлшер-морфология корреляциясын табу тиімді технологиялық жағдайды бағалаудың мәселесін өте терең ұғынуға әкеледі.

Тірек сөздер: оттегі және сутегі плазмасы, золь-гель әдісі, мырыш тотығы, қалайы тотығы.

Резюме

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ВЛИЯНИЕ ОБРАБОТКИ ВОДОРОДНОЙ И КИСЛОРОДНОЙ ПЛАЗМОЙ НА СВОЙСТВА ТОНКИХ ПЛЕНОК SnO_2 И ZnO, СИНТЕЗИРОВАННЫХ ЗОЛЬ-ГЕЛЬ ТЕХНОЛОГИЕЙ

Тонкие пленки SnO_2 и ZnO были синтезированы золь-гель методом. Затем пленки были обработаны O- и H-плазмами тлеющего разряда. Структура, оптические и морфологические характеристики были измерены и проанализированы. Корреляция между размерами кристаллитов и морфологическими характеристиками были выведены на основе компьютерного анализа матрицы данных сканирующего зондового микроскопа (СЗМ). Измерения рентгеновских спектров и спектров оптического пропускания подтвердили компьютерные результаты. Обнаружение корреляции размер-морфологии в тонких оксидных пленках ведет к более глубокому пониманию проблем оценки оптимальных технологических условий для синтезирования тонких оксидных пленок.

Ключевые слова: кислородная и водородная плазма, золь-гель технология, оксид олова, оксид цинка.

Поступила 15.01.2014г.