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Synthesis and Properties of ZnO/Al Thin Films Prepared by Dip-Coating Process

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Abstract **− In this work sol–gel dip-coating technique was used to synthesize ZnO and ZnO/Al films. The influence of annealing regime and dopant concentration on the structural properties of ZnO and aluminum doped ZnO (ZnO/Al) films was investigated. The surface morphology and crystallinity of ZnO films were determined using atomic force microscopy and X-ray diffraction, respectively. The experimental results show that ZnO and ZnO/Al films prepared using "shock" conditions have smooth surfaces and uniform grains. Increase of aluminum concentration led to grain size reduction and denser film.**

Keywords **− ZnO/Al, thin film, dip-coating, annealing conditions.**

I. Introduction

Zinc oxide is a transparent semiconducting oxide with a direct wide band gap (3.37 eV) [1]. ZnO nanoparticles have piezoelectric, electric and optical properties and they also show ultraviolet emission near band gap. Possible applications of ZnO nanoparticles are humidity and gas sensors, photoelements and light emitting diodes [2], varistors [3], surface acoustic wave devices [4], optical waveguides [5], solar cells [6], etc.

High electrical conductivity, optical transparency in wide range and resistance to hydrogen plasma exposure of ZnO films doped with III group elements (B, Ga, In) makes them prospective materials for application in transparent electrodes, optoelectronic devices and solar cells [7], [8].

Doped zinc oxide (ZnO) thin films (including with Al^{3+}) are a promising alternative for indium tin oxide transparent conducting films, due to high conductivity and excellent optical properties. ZnO/Al thin films can be produced by many methods such as chemical vapour deposition [9], radio frequency sputtering [10], sol-gel dip-coating [11], spray pyrolysis [12].

In this work we have studied the structural and optical properties of ZnO/Al thin films prepared by sol-gel dip-coating process.

II. Experimental Section

A. Materials

Zinc acetate dihydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$), diethanolamine (DEA), aluminium nitrate nonahydrate ($Al(NO_3)_3 \cdot 9H_2O$) were obtained from Sigma Aldrich. All the reagents used in the experiments were analytical grade and were used without further purification. During experiments samples with different mole fraction of Al^{3+} were prepared 0 %, 1 % and 5 %.

B. Characterization

The effect of the annealing conditions on the particle size of the synthesized ZnO nanoparticles was studied using powder X-ray diffraction (XRD) with X-ray diffractometer Rigaku Ultima+. Cu Kα radiation was used in XRD. Scanning electron microscopy (SEM) images were obtained using scanning electron microscope T200 - JEOL at an accelerating voltage 5 kV. Atomic force microscopy (AFM) was done using Veeco SPM II microscope in a non-contact mode. AFM measurements were used to investigate the effect of Al^{3+} doping on the microstructure of ZnO/Al films. Al^{3+} doping influence on optical properties of the films was studied using Speccord 210 PC ultraviolet-visible light (UV-VIS) spectrometer.

C. Preparation of ZnO/Al Thin Films

A precursor solution was synthesized by dissolving zinc acetate dihydrate in ethanol and DEA solution. The concentration of zinc ions was 0.5 M, and the molar ratio of DEA to zinc ions was maintained at 1.0. The volume ratio of C_2H_5OH : DEA : $Zn(CH_3COO)_2 \cdot 2H_2O$ was 89 : 5 : 6. The solution was stirred at 60 °C for 2 h to yield a clear and transparent sol. $Al(NO_3)_3 \cdot 9H_2O$ was used as a dopant with mole fraction 0 %, 1 % and 5 % to form ZnO, ZnO/Al-1 and ZnO/Al-5 samples, respectively. After addition of $Al(NO_3)_3 \cdot 9H_2O$, solution was stirred for further 1.5 h. The solution was then aged in room temperature for 24 h. The precursor solution was deposited on Menzel-Gläser sodium silicate glass substrates by dip-coating process. Glass substrates were cleaned using CeO_2, soap, distilled water and ethanol. After coating the substrates were pre-heated at 200 °C for 10 min. Then the films were transformed into nanocrystalline pure or aluminium-doped ZnO films by thermal treatment at 500 °C for 30 min. Two different thermal treatment methods were used: gradual increase of the temperature, with increase rate 5 °C/min, or using "shock" conditions (specimens were inserted in the maximal temperature 500 °C).

III. Results and Discussion

A. Results

The surface morphologies of the ZnO, ZnO/Al-1 and ZnO/Al-5 films measured by AFM are presented in Fig. 1. Two different annealing treatments of ZnO and ZnO/Al films are the gradual increase of the temperature and the "shock" conditions. Fig. 2 shows the surface roughness of the films and Fig. 3 shows

the average grain size of the films. For samples annealed using gradual increase of temperature the surface was relatively rough, they had bigger grain size and inhomogeneous grain distribution along the specimens compared to samples annealed using "shock" conditions. Upon comparison of samples with different amounts of Al^{3+}, it can be seen that temperature treatment method has a significant influence on ZnO/Al surface.

For samples obtained using "shock" conditions, ZnO doping with Al^{3+} led to finer grain sizes. For samples obtained using gradual temperature increase Al^{3+} doping led to an opposite effect.

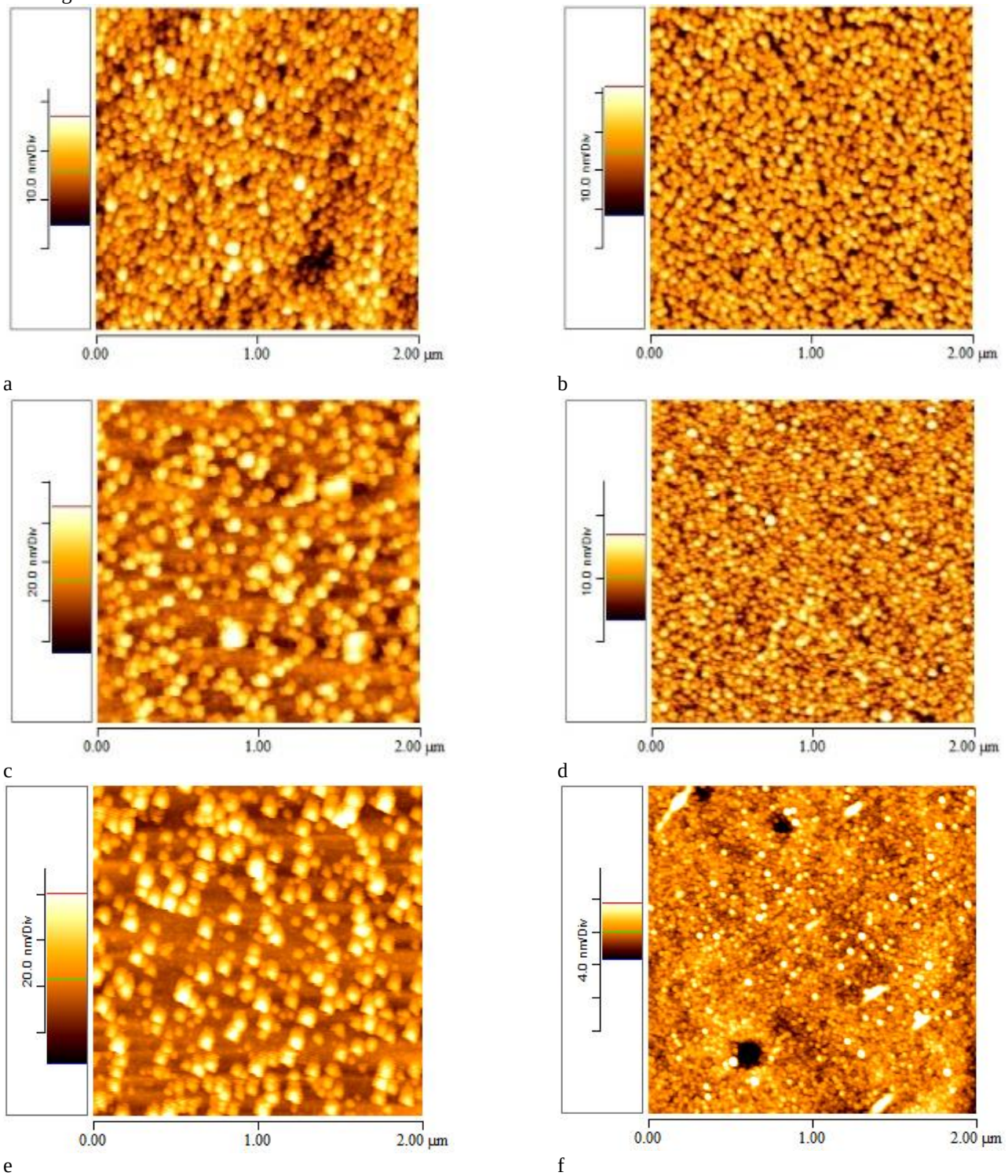

Fig. 1. AFM results showing ZnO (a and b), ZnO/Al-1 (c and d) and ZnO/Al-5 (e and f) film morphology. The films are annealed using different conditions: a), c) and e) gradually increasing temperature by 5 °C/min; b), d) and f) "shock" conditions.

The crystal structures in thin films were identified using XRD. Fig. 4 displays the X-ray diffraction patterns of the samples annealed using "shock" conditions. For both ZnO and ZnO/Al films the patterns corresponded to five diffraction peaks of crystalline ZnO: (100), (002), (101), (102), (110). This indicates that films had a hexagonal wurtzite structure.

Fig. 5 shows optical transmittance spectra of samples ZnO, ZnO/Al-1 and ZnO/Al-5 in range from 300 nm to 740 nm. Upon doping ZnO with Al^{3+} the optical transmittance increased in direct proportion to the changes of Al^{3+} concentration.

Optical transmittance of ZnO sample was 82.28 %. For ZnO/Al-1 sample optical transmittance was 88.45 % and for ZnO/Al-5 sample optical transmittance was 91.03 %.

For investigation of concentration of Al^{3+} influence on film morphology SEM was performed. SEM results are presented in Fig. 6. In SEM images it can be seen that the coatings consisted of individual grains that are densely arranged. Furthermore, with the increase of Al^{3+} dopant concentration, grains were arranged more densely. Pure ZnO film had larger grain size, but narrower grain size distribution, compared to ZnO/Al films. For ZnO/Al films grain size decreased, if Al^{3+} concentration increased.

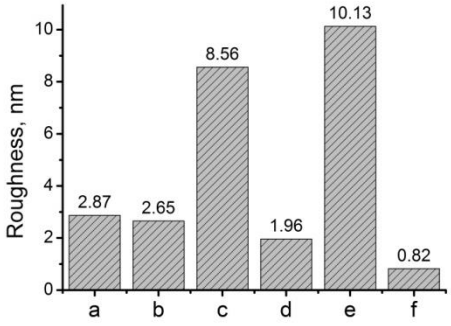

Fig. 2. ZnO (a and b), ZnO/Al-1 (c and d) and ZnO/Al-5 (e and f) film roughness annealed at different conditions: a), c) and e) gradually increasing temperature with increase rate 5 °C/min; b), d) and f) "shock" conditions.

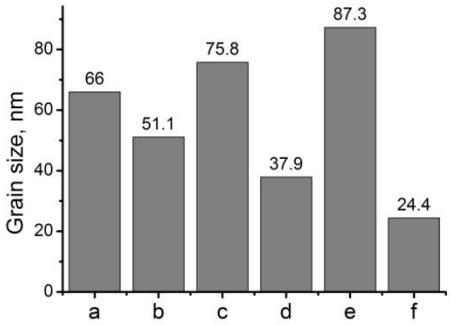

Fig. 3. Grain sizes of ZnO (a and b), ZnO/Al-1 (c and d) and ZnO/Al-5 (e and f) films annealed at different conditions: a), c) and e) gradually increasing temperature with increase rate 5 °C/min; b), d) and f) "shock" conditions.

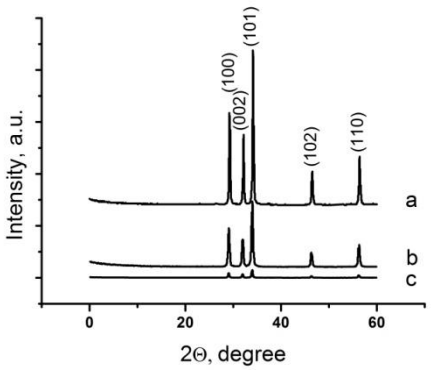

Fig. 4. X-ray diffraction pattern of ZnO (a), ZnO/Al-1 films (b) and ZnO/Al-5 (c).

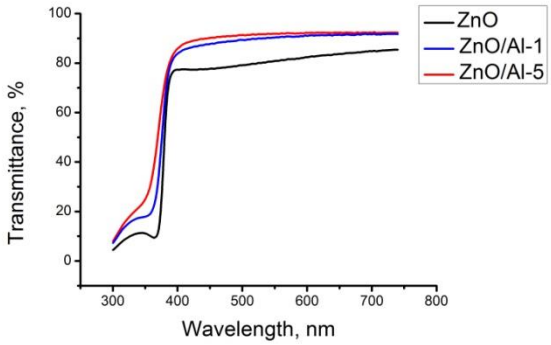

Fig. 5. Optical transmittance spectra of ZnO and ZnO/Al obtained using "shock" conditions.

B. Discussion

The possible reason for higher roughness of samples annealed with gradual increase of temperature (see Fig. 1) is given in the further text. Samples annealed with gradual increase of temperature formed irregular particle size distribution, because the growth of the particles occurs gradually starting from the upper layers and spread in depth, so the particle growth on the surface limited the growth of the particles located in inner layers. Conversely, in coatings, obtained using "shock" conditions, the particle growth occurred uniformly at all film depths. Gradual increase of the annealing temperature also caused crystalline lattice deformation due to anisotropic thermal motion, but when using the "shock" conditions crystal lattice deformation did not have time to take place, when the sample reached the maximum temperature momentarily.

In Fig. 4 XRD results for pure and Al^{3+} doped ZnO films are shown. In both cases there was ZnO wurtzite crystalline phase. The intensities of diffraction peaks of the (100), (002), (101), (102) and (110) planes tended to decrease with entry of Al^{3+} dopant. This indicates that doping with Al^{3+} decreased the crystallinity of ZnO films. In XRD patterns of both ZnO/Al-1 and ZnO/Al-5 no new peaks appeared. This could be caused by interaction between Al^{3+} and ZnO. It may be due to the fact that Al^{3+} upon entering the ZnO structure did not form a

crystalline phase or solid solutions with ZnO system or that the concentration of Al^{3+} is too low.

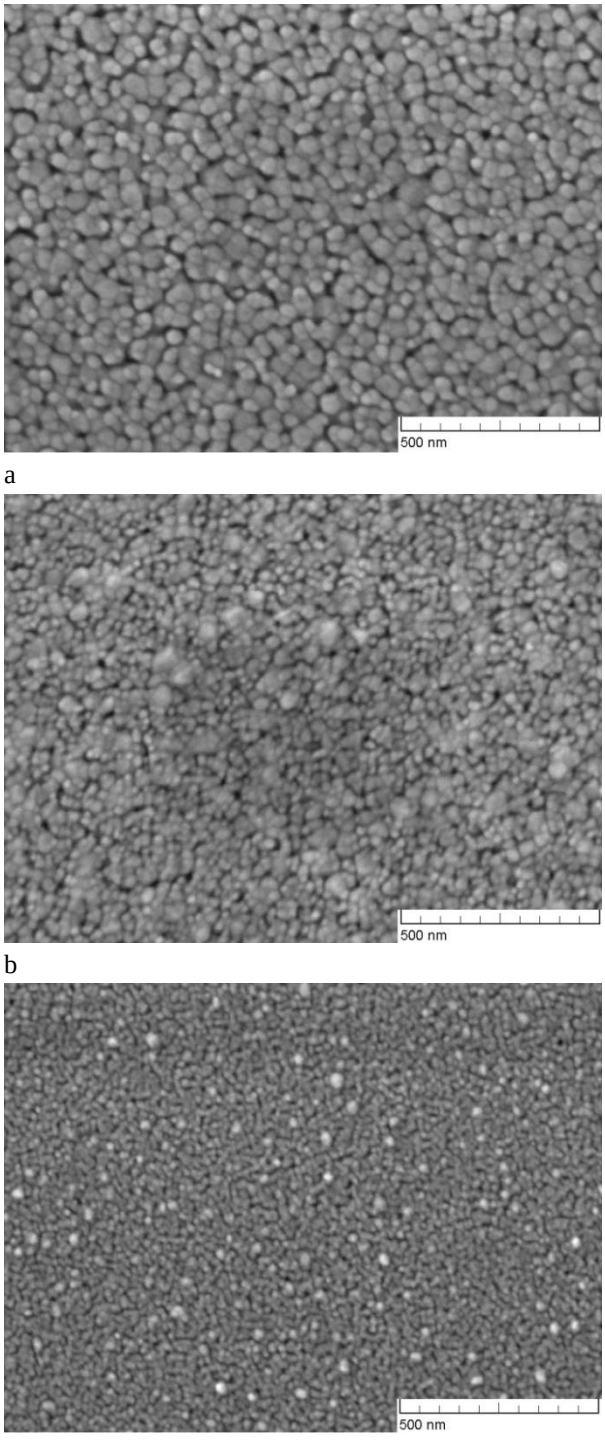

Fig. 6. SEM microscope images of ZnO and ZnO/Al filmsobtained using "shock" conditions: a) pure ZnO film; b) 1 % mole fraction Al^{3+} doped film (ZnO/Al-1); c) 5 % mole fraction Al^{3+} doped film (ZnO/Al-5).

Optical transmittance spectra of samples shown in Fig. 5. It shows that doping of ZnO with Al^{3+} increase the intensity of optical transmittance; this can be explained by decrease of porosity in ZnO/Al samples. Reduction of porosity is explained by the particle size distribution − smaller particles filled in the gaps between larger particles, thus preventing the formation of pores.

SEM images in Fig. 6 show that between the particles pores were formed. This can be determined by both optical and electrical properties of the material. Since the samples doped with Al^{3+} had smaller particle sizes than the ZnO model, the amount of pores in these samples decreased due to the formation of particles in denser arrangement.

IV. Conclusion

ZnO and ZnO/Al thin films were coated on sodium-silicate glass substrate by sol-gel dip-coating method. Influence of annealing conditions on the morphology of thin films was investigated. Surface of the specimens annealed in "shock" conditions had better quality, lower roughness and smaller particle size.

Studies on the effects of the Al^{3+} concentration on ZnO/Al thin film morphology indicated that the increase of Al^{3+} concentration in ZnO composition led to decrease of particle size in the films and formation of denser particle arrangement; this resulted in an increase of optical transmittance.

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Inna Juhņeviča, Marija Mašonkina, Gundars Mežinskis, Aļona Gabrene. ZnO un ZnO/Al pārklājumu iegūšana ar iemērkšanas-izvilkšanas metodi un to īpašības.

Pēdējos gados ZnO plānie pārklājumi ieņēmuši nozīmīgu vietu jaunajās tehnoloģijās. Tiem ir plašs pielietojumu diapazons – gan zinātnē, gan tehnoloģijā. ZnO plānos pārklājumus var izmantot saules baterijās, gāzu sensoros, pjezoelektriskās ierīcēs, kā katalizatorus un vēl daudzās dažādās sfērās. Leģējot cinka oksīdu, ir iespējams izveidot materiālu ar izcilām elektriskajām īpašībām. Kā leģējošos jonus var izmantot I, V un retzemju grupu elementus. No visiem uzskaitītajiem elementiem tieši leģēšana ar Al^{3+} joniem var veicināt struktūru ar defektiem veidošanos, izmainīt optiskās un elektriskās īpašības. Iespējamas vairākas metodes ZnO/Al pārklājumu iegūšanai, piemēram, ķīmiskā tvaika kondensēšana, pulsējošā lāzera nogulsnēšana, uzputināšana un sola-gēla metode. Salīdzinot sola-gēla metodi ar citām metodēm, tās priekšrocības ir nelielas izmaksas un viegli realizējams process.

ZnO un ZnO/Al^{3+} plānos pārklājumus uz nātrija-silikātu stikla virsmas ieguva, izmantojot sola-gēla iemērkšanas-izvilkšanas metodi. Tika noteikta apdedzināšanas režīma ietekme uz plānā pārklājuma morfoloģiju. Paraugu virsma, kuru pakļāva „šoka" apdedzināšanai, bija kvalitatīvākā, bez redzamiem defektiem, ar augstāko raupjuma pakāpi un pārklājumu veidojošās daļiņas bija mazāka izmēra.

Pētījuma rezultāti liecina, ka Al^{3+} jonu ievadīšana ZnO sola-gēla sastāvā izmaina plānā pārklājuma morfoloģiju un īpašības. Al^{3+} jona koncentrācijas paaugstināšana ZnO sola-gēla sastāvā veicina ZnO daļiņu izmēra samazināšanos pārklājumā un blīvāka pārklājuma veidošanos.

Инна Юхневича, Мария Машонкина, Гундарс Межинскис, Алёна Габрене. Получение тонких покрытий ZnO и ZnO/Al методом золь-гель и их свойства.

В последние годы именно тонкие покрытия ZnO занимают значительное место в новых технологиях и покрывают огромный диапазон применения в различных технологиях и науке. Тонкие покрытия ZnO можно использовать в солнечных батареях, сенсорах, пьезоэлектрических установках и других сферах. Легируя оксид цинка, можно получить материал с уникальными электрическими свойствами. Легирующими ионами могут быть элементы I, V группы и редкоземельные элементы. Ионы Al^{3+} могут быть использованы для создания структуры с элементами дефектов, а так же для улучшения оптических и электрических свойств.

Для получения ZnO/Al покрытий могут быть использованы разные методы, например, химическая конденсация из газообразной фазы, осаждение, напыление, а также технология золь-гель. Сравнивая метод золь-гель с другими методами, метод золь-гель имеет преимущества в сравнительно низких затратах и в простате реализуемого процесса.

Тонкие покрытия ZnO и ZnO/Al были нанесены на натрий-силикатную стеклянную подложку методом окунания в растворы золь-гель. Было проверено влияние режима обжига на морфологию тонких покрытий. Поверхность образцов, которые подверглись шоковому режиму термообработки, была более качественная, без видимых дефектов, с вышей степенью шероховатости и частицы, образующие поверхность покрытия, были с меньше по размерам.

Результаты исследования указывают, что введение иона алюминия в состав золей ZnO изменяют морфологию и свойства тонких покрытий. Повышение концентрации иона алюминия в золь-гель ZnO составах ведёт к уменьшению размера частицы покрытия и образованию более плотной поверхности покрытия.