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TOPOLOGICAL FEATURES OF TIN DIOXIDE FILMS OBTAINED FROM THE BIS(ACETYLACETONATO)DICHLOROTIN COMPLEXES

The paper presents the surface morphology studies of tin dioxide nanoscale films produced from Bis(acetylacetonato)dichlorotin complexes of different concentrations. The films are agglomerates of several nanoscale grains. The film's grain size dependence on the number of Bis(acetylacetonato)dichlorotin in the initial solution is established. Dependencies for each type of precursors differ from each other..

Introduction

Thin films of oxide materials with nanoscale grain are widely used as sensors and as transparent electrodes in solar cells and optoelectronic devices. As catalysts for oxidation processes they are used in modern gas analytical industry, besides they are used in device engineering and in electronics [1 – 3]. Liquid phase chemical methods such as a sol-gel method, chemical vapor deposition from a solution, etc. [4, 5] are successfully applied along with the known methods for physical delivery of tin dioxide nanoscale thin film. As far as the decomposition of thermally unstable compounds of tin is the basic process of these methods, the important step is the selection of a suitable precursor.

The preparation method of thin tin dioxide films with nano-sized grains was proposed in our previous works [6, 7]. Aiming to structure the films we used a polymer in the sol-gel process, Bis(acetylacetonato)dichlorotin studied by the authors in [8, 9], which served as the precursor of tin dioxide. Such compounds have been used as precursors, for example, in the preparation of thin films of zirconium dioxide [10]. Complexes of In^{3+} , Sn^{4+} and Sb^{3+} with acetylacetonate were used in [11] as a precursor of oxide films. The sizes of surface irregularities due to morphological studies results are 42 – 125 nm for $\text{SnO}_2\text{:Sb}$ films and 205 – 520 nm for $\text{In}_2\text{O}_3\text{:Sn}$ films. According to X-ray diffractometry data these inhomogene-

ities consist of crystallites with an average size of 25 ± 5 nm for $\text{SnO}_2\text{:Sb}$ films, and 10 ± 5 nm for $\text{In}_2\text{O}_3\text{:Sn}$ films, correspondingly. Properties and structure of studied films are predefined by features of film-forming solutions.

The surface morphology studies of nanoscale tin dioxide films produced of Bis(acetylacetonato)dichlorotin complexes of different concentrations is presented in this paper.

Films' preparation technique and research methods

The film preparation procedure is given in [4]. Bis (acetylacetonato)dichlorotin (BADCT) was used as a tin dioxide precursor [6]. Three complexes of precursor were used in this work. Two of them are based on stannic(IV) chloride (SnCl_4) [7]: the air-dried one is Complex BADCT (IV) N1, and vacuum-dried is Complex BADCT (IV) N2. Besides those we used complex № 3 (BADCT (II)) obtained from stannous chloride dehydrate ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$) [8], which was air-dried.

The sample preparation procedure consisted of several stages: preparation of the polymer solution in acetone, obtaining the precursor solution in acetone, the combination of solutions, film coating, pre-drying at a temperature $\sim 60^\circ\text{C}$, annealing of layers at a temperature 500 – 600°C.

Films were prepared from several solutions with different concentrations of precursors: the complex № 1 – 1, 5, 10% of precursor in the coat-

ing solution, the complex № 2 – 0.5, 1, 2, 4, and 5% of precursor in the coating solution, the complex № 3 – 1, 5, 10% of precursor in the coating solution.

The surface morphology of tin dioxide layers was investigated by the industrial Atomic Force Microscope (AFM) Nano Scope 111 a (Digital instruments, USA). The measurements were fulfilled by siliceous probe with a nominal radius ~10 nm (NT-MDT, Russia) in semi-contact mode (Tapping Mode – TM). The investigated surface area was from 500x500 nm up to 50x50 mkm. AFM NT-206 (Belarus) with Micromasch cantilevers (Germany) was used for Contact Mode measurements.

Experimental results and discussion

Fig.1 presents three dimensional AFM image of tin dioxide films derived of film-forming solutions with different concentrations of complex № 1 precursor (air-dried BADCT(IV)), and the corresponding profiles of the film surface.

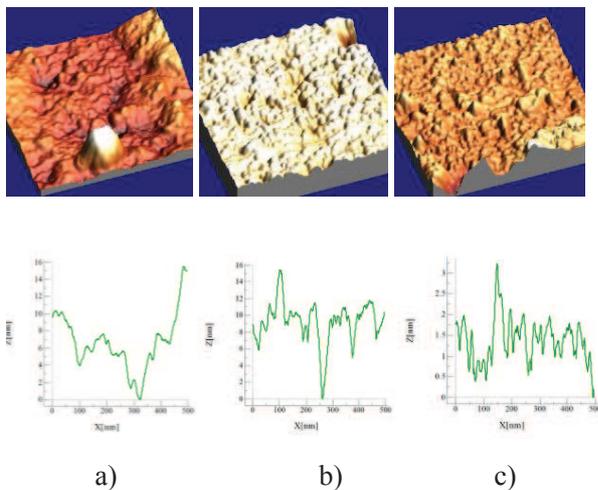


Fig.1. 3-D AFM image of tin dioxide film surface: a) 1%, b) 5% and c) 10% of the complex № 1 in the coating solution (500x500 nm) and the corresponding surface profiles of the samples

As it follows from the film surface profiles, the increasing of the precursor amount in the original film-forming solution correlates with increases of the film's surface roughness. As the precursor concentration decreases (up to 1%) the film shows a developed surface, with large agglomerates ~ 200 nm and with the grain diameter of

~ 20 nm. At 5% of BADCT the surface roughness increases, although the films become more homogeneous. It is seen the reduction in the agglomerate size up to 100 nm, and the grain apparent size is in the range of 15 – 20 nm. At the highest concentration of precursor (10%) in this series of films the decrease in grain size and an increase in surface roughness are observed. Thus, the agglomerates in the film are virtually absent.

The topology of the first series of films is well explained by the peculiarities of the used precursor - hydrated air-dried BADCT(IV) (9). The water in its composition loosens film during annealing and prevents the formation of large agglomerates. Smaller step of roughness is a consequence of loosening in the films in this series. Loosening also leads to decrease the roughness step and increase the unevenness height in films with increasing concentration of the precursor.

Fig.2 shows a 3-D AFM image of tin dioxide films derived from film-forming solutions with different precursor's concentrations of complex № 2 (dried in vacuum BADCT (IV)).

The precursor concentration Studied area 45x45 μm 5x5 μm

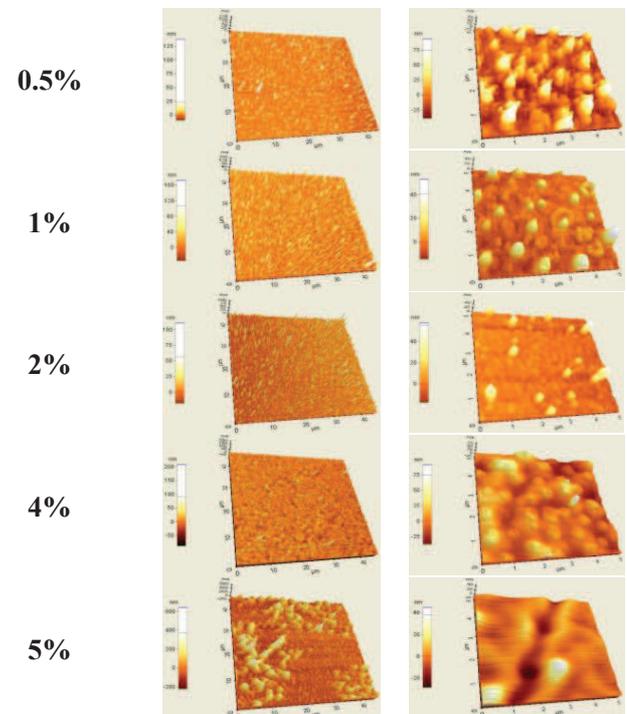


Fig.2 3-D AFM image of tin dioxide films for different concentrations of the precursor № 2 in the coating solution.

As it is evident from Fig.2, there is a correlation between the precursor concentration in the original film-forming solution and the surface roughness of tin dioxide films. At low concentrations of precursor (0.5% and 1%) films have a developed surface and consist of agglomerates of grains with a columnar structure. The agglomerate size varies between 100 – 400 nm. The precursor's concentration increasing gives the film crystallites growth in size, appearance of the cluster structure of the film and the agglomerate size reaches the values ~ 1 mkm.

This series of films has an additional feature. The histogram of the film approximated by Gaussian function (solution of 4%, complex № 2 in [12]) shows that the film consists of two groups of clusters occupying approximately equal space. The first group contains clusters ranging from several nanometers to 200 nanometers size, and the second one covers the cluster sizes more than 200 nm. The presence of two groups of clusters has been confirmed in [12] by the polarization modulation of electromagnetic radiation method (SPR-research). Existence of two groups of clusters, established in [12], is observed in the AFM images of films (see Fig.2).

As it can be seen, the films made of vacuum-dried precursor differ both in grain and agglomerate sizes, and also in the surface development. In the case of a precursor complex № 1 surface development is increased and the agglomerate and grain sizes are decreased. In the case of the precursor complex № 2 the surface development is reduced, and agglomerates' and grains' sizes are increased. Because the precursor is non-hydrated, the second series films have a higher density and do not loosen during annealing. The result is grain coarsening and agglomeration with increasing concentration of the precursor.

Fig.3 shows films' surface images and profiles for the complex № 3 (based on BADCT (IV) films.

The last series images in Fig.3 differ a lot from the previous ones. Prepared from solutions with the smallest amount of precursor BADCT (II) films have the cluster-like structure with cluster size of 60 – 80 nm. Presented images don't allow to suppose the structure of the cluster. At higher concentrations of the precursor (5%), the cluster size significantly decreases (20 – 50 nm), but the

surface roughness is not substantially increased. At the concentration of precursor equal to 10% the cluster size increases up to 100 nm, wherein the surface roughness also increases. It can be seen that clusters of this film series have a petalous shape, unlike clusters of another film series. Cluster form may be determined by the existing direction of crystallite growth in the film derived from the solution containing the precursor complex № 3.

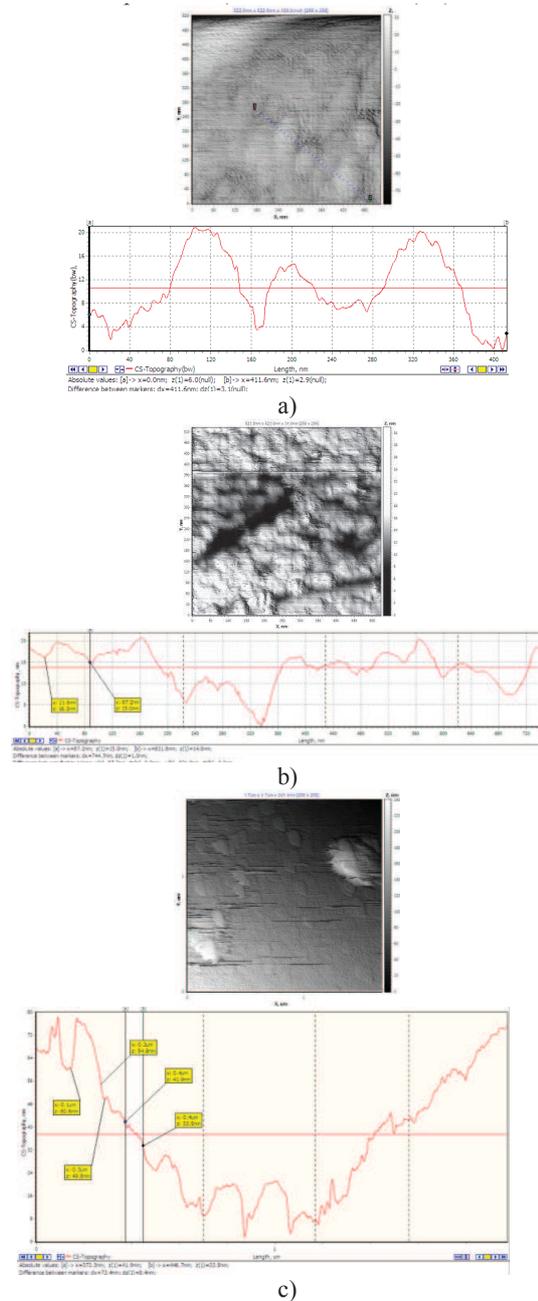


Fig.3. AFM image of the surface of the films obtained from solutions containing: a) 1%, b) 5%, and c) 10% of BADCT (II).

Conclusion

Studies of tin dioxide films established a correlation between their surface morphology and concentration of tin dioxide precursor in the coating solution. However, this correlation is not one the same for all three types of precursors. Consequently, not only the quantity of the precursor in the coating solution determines the structure type (and hence different physical properties of films), but also the precursor preparation process.

References

1. D. S. Ginley, H. Hosono, D. C. Paine (Eds.), Handbook of Transparent Conductors, Springer Science+Business Media, New York, 2010.
2. J. Huang and Q. Wan. Gas Sensors Based on Semiconducting Metal Oxide One-Dimensional Nanostructures Sensors 2009, 9, 9903-9924; doi:10.3390/s91209903.
3. M. Batzill, U. Diebold. Progress in Surface Science, 79, 47 (2005).
4. J. Gong, Q. Chen. Sol-Gel Prepared Single Wall Carbon Nanotube SnO₂ Thin Film for Micromachined Gas Sensor// Nanotech. – 2004. – Vol. 3. – P. 232 – 235.
5. В. В. Иванов, И. А. Сидорак, А. А. Шубин, Л. Т. Денисова. Получение порошков SnO₂ разложением термически нестабильных соединений // Journal of Siberian Federal University. Engineering & Technologies. – 2010. – Vol. 2, №3. – P. 189-213.
6. Filevskaya L. N., Smyntyna V. A., Grinevich V. S. Morphology of nanostructured SnO₂ films prepared with polymers employment// Photoelectronics. - 2006. - №15. – P.11-14.
7. V. S. Grinevych, V. A. Smyntyna, L.M. Filevska. Influence of a precursor properties on the surface morphology of nanoscale tin dioxide films. Photoelectronics. Odessa. 21 (2012), P. 13-17.
8. B. Ulug, H. M. Türkdemir, A. Ulug, O. Büyükgüngör, M.B. Yücel, V.A. Smyntyna, V.S. Grinevich, L.N. Filevskaya. Structure, spectroscopic and thermal characterization of bis(acetylacetonato)dichlorotin(IV) synthesized in aqueous solution // Ukrainian chemical journal. – 2010. – Т. 76, №7. – С. 12-17.
9. В. С. Гриневич, В. А. Смынтына, С. Н. Савин, Л. Н. Филевская, Б. Улуг, М. Х. Туркдемир, А. Улуг, С. Ялткая. Термогравиметрические исследования комплексов прекурсора для получения наноразмерных пленок двуокиси олова. Сенсорная электроника и микросистемные технологии. 2011, № 2. – С.69-75.
10. Борило Л. П. Синтез и физико-химические закономерности формирования золь-гель методом тонкопленочных и дисперсных наноматериалов оксидных систем элементов III-V групп. Автореферат диссертации на соискание ученой степени доктора химических наук. – Томск. 2003. – 29 с.
11. С. А. Кузнецова, Т. Д. Малиновская, В. И. Сачков, Влияние строения комплексных частиц в пленкообразующем растворе на структуру и свойства пленок In₂O₃:Sn и SnO₂:Sb. Известия Томского политехнического университета. 2004. Т. 307. № 2, с.105-108.
12. V.S. Grinevich, L. M. Filevska, I. E. Matyash, L. S. Maximenko, O. N. Mischuk, S. P. Rudenko, B. K. Serdega, V. A. Smyntyna, B. Ulug. Surface plasmon resonance investigation procedure as a structure sensitive method for SnO₂ nanofilms. Thin Solid Films 522 (2012) 452–456.

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Abstract

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Keywords: tin dioxide, Bis(acetylacetonato)dichlorotin, thin film, surface morphology.

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ТОПОЛОГИЧЕСКИЕ ОСОБЕННОСТИ ПЛЕНОК ДИОКСИДА ОЛОВА, ПОЛУЧЕННЫХ ИЗ КОМПЛЕКСОВ ДИХЛОРДИАЦЕТИЛАЦЕТОНАТА

Аннотация

В работе представлены результаты исследований морфологии поверхности наноразмерных пленок двуокиси олова, полученных из комплексов дихлордиацетилацетоната олова различной концентрации. Пленки состоят из агломератов нескольких зерен наноразмера. Установлена зависимость размера зерна в исследуемых пленках от количества дихлордиацетилацетоната в исходном растворе для их получения. Зависимости для каждого из типов прекурсоров отличаются друг от друга.

Ключевые слова: диоксид олова, дихлордиацетилацетонат олова, тонкие пленки, морфология поверхности.

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ТОПОЛОГІЧНІ ОСОБЛИВОСТІ ПЛІВОК ДІОКСИДУ ОЛОВА, ОТРИМАНІХ З КОМПЛЕКСІВ ДІХЛОРДІАЦЕТИЛАЦЕТОНАТА

Анотація

У роботі представлені результати досліджень морфології поверхні нанорозмірних плівок двоокису олова, отриманих з комплексів діхлордіацетилацетоната олова різної концентрації. Плівки складаються з агломератів декількох зерен нанорозміру. Встановлено залежність розміру зерна в досліджуваних плівках від кількості діхлордіацетилацетоната у вихідному розчині для їх отримання. Залежності для кожного з типів прекурсорів відрізняються одна від одної.

Ключові слова: діоксид олова, діхлордіацетилацетонат олова, тонкі плівки, морфологія поверхні .