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INFLUENCE OF A PRECURSOR PROPERTIES ON THE SURFACE MORPHOLOGY OF NANOSCALE TIN DIOXIDE FILMS

The work presents the results of the nanosize tin dioxide films' surface morphology investigation which is dependent on the precursor complex's technological properties used for their production. The used precursors differ only due to the technology of their preparation at the final stage. This defines the presence of the bound water in their composition. The water acts as a looser at the thermal decomposition which gives the possibility to obtain the nanosized films with nano grains of different sizes dependently on the precursor's type.

INTRODUCTION

Thin films of oxide materials with nano-sized grains are widely used as sensors in modern gas analyzers, the transparent electrodes for solar cells, catalysts of the oxidation processes [1-3]. The well-known production method for nano-size tin dioxide, as well as other metal oxides, for sensitive elements of sensors are liquid-phase chemical methods: sol-gel method, chemical precipitation from solution, etc. [4,5] The basic process for such technologies is the decomposition of thermally unstable tin compounds to form tin dioxide as the final product. The small number of such compounds, as well as limited and contradictory literature data on their physical and chemical properties causes the necessity for selection of a suitable precursor for nanosized tin dioxide.

In [6] we have proposed a technique for obtaining SnO_2 films based on the method of chemical precipitation from solution using polyvinyl acetate (PVA) as structuring agents. The films investigated in the present work were obtained by this method. Complex based on Bis(acetylacetonato)dichlorotin (BADCT) served as a precursor of tin dioxide. According to [7] this compound ($Sn(C_5H_7O_2)_2Cl_2$) was firstly obtained in 1903. In the literature [8-10] obtaining BADCT was reported using chloroform or dry toluene [9] as a solvent. The peculiarity of our method is using of water as a solvent. Characterization of BADCT obtained by our method is shown in [11].

In [12] it was reported on preparation of ZrO_2 thin films using such compounds, namely, zirconium acetylacetonate. Using a BADCT based complex prepared by our original method gives a thin transparent film of tin dioxide with nano-sized grains [13]. Precursor complexes necessary for comparative studies were obtained by two methods, differing only at the latest technological stage: the drying process. A comparative study of these precursor complexes were fulfilled using thermogravimetric methods [13]. Supposedly the different drying processes determine conservation of water molecules in the precursor complex which influences the structure and morphology of the resulting film. The principal goal of the present work is the investigation of the mentioned precursor's peculiarities influence on the surface morphology of the obtained tin dioxide films.

METHODS OF FILMS PRODUCTION AND INVESTIGATIONS

Samples for the investigation were prepared by the technique described in [6]. Bis(acetylacetonato)dichlorotin (BADCT) was used as a tin dioxide precursor [11]. Initially it was a preparation of the precursor: the production solution N1 was prepared of 50 ml (0,5 mol) of

acetilaceton dissolved in 250 ml of the distilled water and then put away for 24 hours for full dissolution. Next, the production solution N2 was prepared of 14ml (0,12 mol) of tin tetrachloride and 50 ml of cold (2-5°) distilled water. Further, the production solutions N1 and N2 were mixed adding 5 ml of 20% of aqueous NH_3 solution. The mixture obtained was being mixed for two hours by the magnetic mixer which resulted in deposition of thick white sediment. 600 ml of distilled water was added to it. After 10-15 minutes of settling the upper layer was decanted. The sediment was separated by the vacuum filtering by the Shott filter (residue pressure P = 500 mm Hg) then washed by the distilled water and dried up at 20-25°C during 3 days. Finally, it was washed by benzyl and dried up for 5-6 hours at 60°C: complex N1 in the air, and complex N2 — in vacuum.

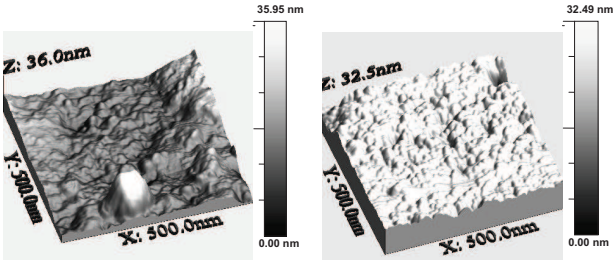
This difference of these two complexes has become their principle production peculiarity which was investigated in the present work due to its influence on the topology properties of the films.

Freshly prepared BADCT was dissolved in acetone at different concentrations, then equal volumes of each solution were mixed with the same volumes of Polyvinlyacetate (PVAC) solutions in acetone prepared at different PVAC concentrations. The mixtures were then sprayed onto the microscope cover glass of 22 mm x22 mm size. Samples were kept at room temperature for about 15 minutes to allow the removal of acetone prior to annealing them at 600 °C for 6 hours in air for the thermal decomposition of organic components of the film (BADCT and PVAC) and subsequent removal of decay products. Removal of organic components was confirmed by our thermogravimetric studies of the precursor [11] and by the data [14] on the PVAC decomposition at temperatures above 200 °C, particularly in the presence of catalytic oxides (tin dioxide in our case). After annealing, the tin dioxide film was left on the substrate. PVAC was employed to structurize the film during the removal of its decay products.

The tin dioxide layer's surface morphology was investigated by the industrial Atom Force microscope (AFM) Nano Scope 111a (Digital instruments, USA). The measurements were fulfilled by siliceous probe with a nominal radius ~10 nm (the production firm NT-MDT, Russia) in a regime of periodical contacts (Tapping Mode™). The investigated surface area was in the interval of 500x500 nm^2 to 45x45 mkm^2.

RESULTS AND DISCUSSION

Figure 1 shows the AFM-image of the tin dioxide films surface morphology obtained from the precursor complex number 1. The higher points at Fig. 1, correspond to the lighter parts of the snapshot, the dark parts reflects the deeper zones. Amount of precursor in the initial solution was 1 and 5 wt %.



a b

Fig. 1. AFM-images of the surface morphology of tin dioxide films obtained from precursor complex number 1. The content of the precursor in the original solution: a — 1 wt %, b — 5 wt %.

As it can be seen from the images obtained for the complex number one, the film of tin dioxide has a well-developed surface and structured at a nanoscale. The minimal grains' size, visible in the images is in the interval from 10 to 15 nm. One may notice that the films' thickness visually evaluated increases with the precursor's concentration increasing.

Figure 2 shows the AFM-images of the surface of tin dioxide films obtained from precursor complex number 2 (dried in vacuum). As in the previous case, the precursor's content in the initial solution was 1 and 5 wt%.

As it can be clearly seen at the figures, the films have developed surfaces and are composed of agglomerate groups of different sizes, mostly of columnar structure. The crystallites grain sizes in the films (precursor number 2) is an average from 200 nm (at lower concentrations) to 500 nm and more (with a greater concentration of the precur-

sor), which is in strict correspondence with AFM image scaling. Consequently, there is a definite dependence of the morphology and grain sizes in the films on the concentration of the initial solutions for films obtained. The high concentrations of tin dioxide precursor in the films gave the larger crystallites.

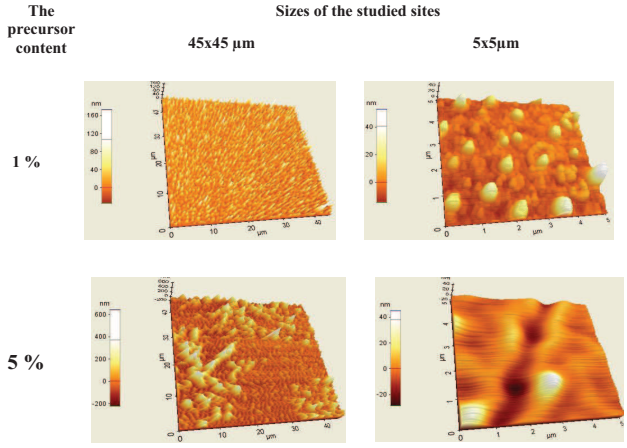


Fig. 2. AFM-images of the surfaces of tin dioxide films obtained from precursor complex number
2. The precursor content and the sizes of the studied sites are indicated.

The images of Figures 1 and 2 comparison shows that the hydrated precursor (complex number 1) gives films with smaller grain size of 10-20 nm. At the same time, the grain sizes of the films obtained from a complex number 2 (anhydrous DHDAO) were 200-500 nm. Hence, the present studies support the idea that a complex of hydrated precursor is preferable in production of tin dioxide films of smaller (nanoscale) grain size, and therefore the more developed surface morphology.

CONCLUSION

The studies of tin dioxide films' surface morphology obtained from two different precursor complexes had established a significant effect of even small differences in the process of obtaining of tin dioxide precursor on the morphology of the surface and structure.

It was found that differences in the drying process used in the production of precursor complexes' films are the significant factor in the topological features of the films. The main feature which defines this influence is the bound water in the precursor's composition.

At the complex thermal decomposition, the water, which is in its composition acts as a loosener, which allows to obtain tin dioxide films with nanograins of different sizes, depending on the precursor's type. Consequently, the use of a complex containing a hydrated precursor (№ 1) should be preferable in obtaining nano-sized tin dioxide films with a well-developed surface, thus providing high sensitivity of its physical parameters to the environmental changes and, and therefore, widely used as sensors.

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Abstract.

The work presents the results of the nanosize tindioxide films' surface morphology investigation which is dependent on the precursor complex's technological properties used for their production. The used precursors differ only due to the technology of their preparation at the final stage. This defines the presence of the bound water in their composition. The water acts as a looser at the thermal decomposition which gives the possibility to obtain the nanosized films with nano grains of different sizes dependently on the precursor's type.

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

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ВЛИЯНИЕ ОСОБЕННОСТЕЙ ПРЕКУРСОРА НА МОРФОЛОГИЮ ПОВЕРХНОСТИ НАНОРАЗМЕРНЫХ ПЛЕНОК ДИОКСИДА ОЛОВА

Аннотация.

В работе представлены результаты исследований морфологии поверхности наноразмерных пленок двуокиси олова в зависимости от особенностей получения комплексов прекурсора для их полученияИспользованные прекурсоры различаются только особенностями приготовления на последнем этапе, что определяет различное содержание в их составе связанной воды. При термическом разложении комплекса вода в его составе выполняет функцию разрыхления, что позволяет получать пленки двуокиси олова с нанозернами разного размера в зависимости от типа прекурсора.

Ключевые слова. двуокись олова, дихлордиацетилацетонат олова, тонкие пленки, морфология поверхности.

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ВПЛИВ ОСОБЛИВОСТЕЙ ПРЕКУРСОРУ НА МОРФОЛОГІЮ ПОВЕРХНІ НАНОРОЗМІРНИХ ПЛІВОК ДІОКСИДУ ОЛОВА

Анотація.

У роботі представлені результати досліджень морфології поверхні нанорозмірних плівок двоокису олова в залежності від особливостей отримання комплексів прекурсора для їх отримання. Використані прекурсори розрізняються тільки особливостями приготування на останньому етапі, що визначає різний зміст у їх складі зв'язаної води. При термічному розкладанні комплексу вода в його складі виконує функцію розпушення, що дозволяє отримувати плівки діоксиду олова з нанозернами різного розміру в залежності від типу прекурсора.

Ключові слова: двоокис олова, діхлордіацетілацетонат олова, тонкі плівки, морфологія поверхні.