The concept of the phases ratio control during the formation of composite filamentary nanocrystals $x$InSe-$\left(1-x\right)$In$_2$O$_3$ on glass substrates

S A Gasanly$^2$, V V Tomaev$^{1,2}$, T V Stoyanova$^2$

$^1$ Institute of Chemistry, Saint-Petersburg State University Saint-Petersburg, 198504, Russia
$^2$ Department of General and Applied Physics, Saint-Petersburg Mining University, Saint-Petersburg, 199106, Russia

Abstract. The method of vacuum deposition on substrates of glass marks the C-29 series PbSe deposited film and the film In in the area 3x3 mm$^2$ and a thickness of ~1 μm. Films are oxidized in dry air at a temperature of 550 °C. Based on studies by X-ray microanalysis and scanning electron microscopy shows the principal possibility of formation of nanowires $x$InSe-$\left(1-x\right)$In$_2$O$_3$ on the PbSe/In structure. The results allowed to formulate the concept of the control of phases ratio in the forming nanowires $x$InSe-$\left(1-x\right)$In$_2$O$_3$ on glass substrates.

1. Introduction

Metal oxide nanostructures with a one-dimensional morphology surface are of great importance both in fundamental and applied fields of use [1]. In comparison with the other forms of nanostructures the dimensional ones have several advantages such as extremely high ratio of surface to the largest volume of nanowhiskers, excellent stability due to its high degree of crystallinity of the individual elements, multifunctional surface, the possibility of the obtaining of transistor structure in the presence of the field effect at the surface, and etc. [2].

The fundamental interest in InSe is due to the display of the diverse unique photoelectric properties [3-6]. The practical use of layered InSe as a material for various areas of electronics is also very promising [7-12]. Another semiconductor wide-gap indium oxide (In$_2$O$_3$) due to a combination of high electrical conductivity and optical transparency is of great scientific interest and widely applied as a transparent electrode, antireflection coating, passivation layer in optoelectronic devices, and also as a sensitive layer in gas sensors [13-15] etc. A biphase composite based on these indium compounds (InSe and In$_2$O$_3$) is in demand in fundamental and applied research as well [16, 17]. The purpose of this paper was the synthesis of composite material by an original method based on the In-Se-O system on glass substrates with the ability to control the ratio of the components (InSe and In$_2$O$_3$).

2. Materials and methods

PbSe film with area 3x3 mm$^2$ and thickness of 1.0 - 1.5 μm was applied on the type C-29 glass substrate. Indium layer with thickness of ~1.6 μm (Figure 1), was deposited on the PbSe film. The films were oxidized in dry air at a temperature of 550 °C. Using the SEM method the surface and chip both the origin films and the oxidized ones have been studied. With X-ray microanalysis method the
qualitative and quantitative assessment of the elemental composition in the subsurface area of the investigated films has been carried out.

![Figure 1. Scheme of the deposited on the glass substrate films](image)

3. Thermodynamic analysis.

When lead selenide is heated at 363 °C above the solid phase of PbSe, the vapor pressure of selenium (Se) ~ 1 mm Hg is reached, while the vapor pressure of lead (Pb) and lead selenide (PbSe) is less a lot than of the magnitude compared with the pressure of selenium vapor [18, 19].

When the double-coated film consisting of PbSe and In films is heated up to 550 °C, the indium layer transforms into liquid state (the melting point of indium is 156.4 °C [20]). While abundant selenium from the solid lead selenide changes into a liquid film, Indium reacts with the chemical reaction and diffuses to the external surface of indium, interacting further with oxygen.

Figure 2 shows the In–Se diagram constructed from the literature review [21-23]. The investigations have been carried out by differential thermal, microstructural and X-ray analysis methods and a microhardness measurement method. Alloys were synthesized in evacuated quartz ampules using In and the simple Se with the purity above 99.9% (by the weight).

The compound In\textsubscript{2}Se is metastable, melts incongruently, and has a high volatility; and the In\textsubscript{5}Se\textsubscript{3} and In\textsubscript{2}Se\textsubscript{3} melt congruently at the temperatures of 660 and 900 °C, respectively. The system has established the existence of four compounds: In\textsubscript{2}Se, InSe, In\textsubscript{5}Se\textsubscript{6}, and In\textsubscript{2}Se\textsubscript{3}. The In\textsubscript{2}Se and In\textsubscript{5}Se\textsubscript{3} compounds have been developed with the help of peritectic reactions at 540 and 660 °C, respectively, and are highly volatile. Solid solutions based on In and Se are practically absent. Both these components form degenerate eutectics: (In) + In\textsubscript{2}Se at the temperature of 156 °C and (Se) + β-In\textsubscript{2}Se\textsubscript{3} at the temperature of 219 °C. The value of the latter temperature is indicated to be lower than in the original works (225 °C), in accordance with the adopted lower (at 6 °C) melting point of Se equal to 221 °C.

In the In-rich alloys, incompatibility in the liquid state takes place. The polymorphic transformations of compounds In\textsubscript{5}Se\textsubscript{6} (β ↔ α at 550 °C) and In\textsubscript{2}Se\textsubscript{3} (β ↔ α at 200 °C, γ ↔ β at 650 °C, δ ↔ γ at 750 °C) have been discovered in the papers [21-23]. The presence of a polymorphic transformation in the compound In\textsubscript{5}Se\textsubscript{6} of the paper [22] has not confirmed. The course of the liquidus line from the Se side at high temperatures, namely the practically horizontal portion at 770 °C, suggests that in this concentration range, a second exfoliation in the liquid state in the system can take place. However, according to [21-23], in these alloys the formation of two layers in the liquid state has not been observed.

The analysis of the phase diagram T-x, for the In-Se system [21-24] presented in the Figure 2. The technological conditions of heat treatment at 550 °C in an dry air atmosphere of liquid indium with gaseous selenium and then with the subsequent cooling to room temperature indicate the formation of InSe and In\textsubscript{5}Se\textsubscript{3} compounds inside the indium liquid film with limited access to oxygen.

In the region of rich in In alloys (the left side of the diagram, see Figure 2), incompatibility in the liquid state takes place. The course of the liquidus line on the Se side (the right-hand side of the diagram, see Figure 2) has a practically horizontal section at 770 °C at high temperatures, which suggests that in this concentration range the second layering in the liquid state in the system may take place [21 - 24].
To complete the picture associated with the oxidation of the two-layer PbSe and In film at 550 °C in the dry air atmosphere, it is also necessary to take into account the possibility of chemical interaction of indium at the interface with air oxygen under these conditions.

![Figure 2. The state diagram of the In-Se system [21].](image)

In the interaction of In with O, the formation of In$_2$O, InO, and In$_2$O$_3$ compounds with an O O – 6.52, 12.24, and 17.30% (by mass) was established [21]. The most stable oxide in this series is In$_2$O$_3$, which has two modifications, with a body-centered cubic and trigonal structure.

In$_2$O$_3$ with the trigonal structure of corundum type was obtained by the hydrothermal method and, it appears, to be a metastable phase formed at high pressures (lattice parameters in hexagonal system: $a = 0.549$ nm, $c = 1.452$ nm, Pearson symbol hP10, $R\bar{3}c$. The cubic modification of In$_2$O$_3$ is isostructural one with Mn$_2$O$_3$ (Pearson symbol cI8, space group Ia3) $a = 1.012$ nm. An increase in the parameter of the body-centered cubic lattice In$_2$O$_3$ from 1.0119 nm at 30 °C up to 1.0199 nm at 968 °C was distinguished.

4. Results and discussion.

The sequence of changes on the surface of the two-layer film is shown using a Zeiss Supra 40VP scanning electron microscope in the Figure 3. The comparison was made with the original film.

![Figure 3(a, b, c). Surface of the initial sample PbSe/In (a) and oxidized at 550 °C samples PbSe/In for t=30 min (b) and t=60 min (c).](image)

Fragments of the initial surfaces in the (Figure 3(a)) and oxidized at 550 °C for 60 (Figure 3(b)) and 120 min (Figure 3(c)) of the two-layer films of lead and indium selenide have been presented in photomicrographs. For all three cases, the formed islets of indium on the surface of both the initial and oxidized films are visible. Compared with the initial surface of the film (Figure 3(a)) on the film surface, an oxidized at 550 °C for 60 min (Figure 3(b)), the precipitates can be observed, similar droplet size ranges 150±250 nm.
The X-ray spectral analysis data for the film oxidized at 550 °C for 120 min, with the choice of the analyzed region at the point on the surface of the island In was shown in the Figure 4 as well.

Figure 4(a, b, c). Express analysis of the elemental composition of two-layer PbSe/In films oxidized at 550°C for 120 min with the choice of the analyzed points: on the surface of the "island" - (a); In the troughs (b); and at the point of the nanowires - (c).

The elemental composition in the selected region consists of oxygen atoms, selenium, lead and indium. In the temperature range 470-610 °C, lead selenite decomposes to form gaseous selenium dioxide and 2PbO-PbSeO₃ and 4PbO-PbSeO₃ compounds. With a long exposure (120 min), there is interaction of selenium dioxide with indium and indium oxide. Figure 4(b) shows X-ray spectral analysis data for the film oxidized at 550 °C for 120 min, with the choice of the region to be analyzed on the surface of the In film at the troughs point. The phase analysis in the investigated point showed the presence of lead oxide and indium oxide.

Figure 4(c) presents X-ray spectral analysis data for the two-layer film oxidized at 550 °C for 120 min with a choice of the point where the nanowires are located. It can be seen that the elemental composition at the selected point includes the oxygen atoms, selenium and indium atoms. By the value of the elements mass values, it can be assumed that the composition of the nanowires includes indium indium selenide and indium oxide, the content of indium selenide being much lower than that of indium oxide.

According to the results of X-ray microanalysis, there are atoms of indium, selenium and oxygen in the spectrum of whiskers. The investigation of individual nanowires was carried out. After mechanical removal from the sample surface and ultrasonic dispersion in an organic solvent, the whiskers precipitated on a graphite substrate were carried out.
X-ray microanalysis spectra taken from the surfaces of individual nanowires were recorded at accelerating voltages of 10, 15 and 20 kV (Figure 5(a, b, c)).

The length of the nanowire is ~ 1.6 μm, and the diameter is ~ 90 nm. It can be seen that the elemental composition of the nanowire surface for three different points at the beginning, middle and end of the filament is the same and consists of the atoms of oxygen, selenium and indium. A large background signal coming from the substrate and bonded to the carbon atom was not taken into account.

![Image](image1.png)

(a)

![Image](image2.png)

(b)

![Image](image3.png)

(c)

**Figure 5(a, b, c).** The analysis of the elemental composition of a whisker crystal deposited on a graphite substrate, with the choice of the analyzed region at the point.

Examinations showed that the mass quantity of each element for each point has the same value within the error of measurement. From the X-ray spectral analysis data, the mass values of the elements were determined, which turned out to be equal to: In – 36±13%; Se – 4±2%; O – 60±15.

In thermal oxidation result of indium and thermal oxidation of lead selenide to lead selenite and its further decomposition, the upper layer of indium in the initial film was transformed into filamentary crystals of composition (1-x)In$_2$O$_3$ – xInSe with the range of x variation from 0.10 to 0.15, and the lower layer of lead selenide was transformed into a friable and thicker layer consisting of lead selenite and lead monoxide. The material consists of a number of disoriented filamentary nanocrystals (1-x)In$_2$O$_3$·xInSe with a range of x variation from 0.10 to 0.15, which are mounted in the matrix of the composite consisting of indium oxide, selenite and lead oxide.
5. Conclusions
It was shown that nanowhiskers xlnSe-(1−x)In₂O₃ were formed on the surface of the films by oxidation at a temperature of 550 °C. Sensor material that consists of a mixture of selenium and indium oxides possesses high gas sensitivity to different liquids and gases.

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