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The Structure and Electrical Properties of $(In_2O_3/SiO_2)_{25}$ Thin Films

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Abstract

Multilayer thin-film structures $(In_2O_3/SiO_2)_{25}$, consisting of alternating layers of nanocrystalline In_2O_3 and amorphous SiO_2, were obtained by ion-beam sputtering. The thickness of the obtained samples varied from 138 to 200 nm. With an increase in the thickness of the $(In_2O_3/SiO_2)_{25}$ bilayer from 5.5 to 8 nm, a monotonic decrease in the electrical resistivity is observed from $8.89 \cdot 10^{-2}$ Ohm·cm to $1.40 \cdot 10^{-2}$ Ohm·cm, which is associated with an increase in the contribution to electric transport layers of In_2O_3 and a decrease in the effect of charge carriers scattering at the In_2O_3–SiO_2 interfaces. The analysis of the temperature dependences of the electrical resistivity in the temperature range 77–300 K has shown that a logarithmic dependence is observed up to 150 K, which is associated with the presence of quantum corrections for electrical conductivity (weak localization of charge carriers) above 150 K and the electricity transfer becomes delocalized charge carriers.

It was established that after vacuum heat treatment at a residual pressure $P_{res} = 5 \cdot 10^{-2}$ Torr, the multilayer structure of thin films $(In_2O_3/SiO_2)_{25}$ is retained up to a temperature of 723 K. In this case, the average crystallite size of In_2O_3 does not exceed the equivalent thickness of the bilayer, and the SiO_2 layers remain in an amorphous state. The value of electrical resistivity after heat treatment decreases to $\rho \sim 2 \div 4 \cdot 10^{-3}$ Ohm·cm at room temperature. Based on the results of the studies, it was concluded that synthesized films $(In_2O_3/SiO_2)_{25}$ can be used as stable channels of thin-film transistors in transparent electronics.

Keywords

Thin films; multilayer structures; oxide semiconductors; thermal stability.

Introduction

Films based on semiconductor metal oxides are of great interest to the scientific community due to their high transparency (~ 90 %) in the visible range and the ability to conduct electric current [1–3]. The oxides presented are used in the manufacture of thin displays, organic light-emitting diodes, solar panels, thin-film transistors, gas sensors, spacecraft, etc. [4–6].

Thin films of In_2O_3 and compounds based on it [7–9], which have a small electrical resistance ($\rho \sim 10^{-4}$ Ohm·cm or less) and a large band gap ($E_g = 3.36$ eV), are most widely used among transparent oxides. The possibility of practical application of In_2O_3 thin films depends not only on their optical and electrical properties: these parameters must be combined with stability to environmental influences, resistance to abrasion, low electron work function, compatibility with the substrate, and other requirements imposed on the transparent semiconductor thin film depending on their application.

The properties of indium oxide and compounds based on it are determined primarily by the presence of oxygen vacancies, the number of which can be controlled either by introducing oxygen during the synthesis of the material or by heat treatment of the films in an oxidizing atmosphere [10]. Secondly, it is necessary to control the structural state (amorphous or crystalline), which is achieved by introducing special elements – amorphizers. These include atoms of Sn, Ta or other alloying elements [10].

Despite the active use of wide-gap amorphous oxide semiconductors and solid solutions based on them as the TFT channels, the instability and fragility of the operating characteristics in single-layer TFT channels arising under the influence of various conditions (temperature, bias voltage, illumination) are some of the key drawbacks in practical application of transparent conductive oxides. The reason for this instability is oxygen vacancies. At the same time, it is known that charge carriers in transparent oxide semiconductors are provided with defects associated with oxygen, and, therefore, the density of oxygen vacancies determines the electrical properties of oxide semiconductors. Thus, a situation arises when you have to choose between stability and poor performance.

The problem can be solved by using multilayer structures as a TFT channel material with high carrier mobility and high performance stability. In recent years, it has been proposed to use multilayer heterostructures consisting of layers from oxide semiconductors as channels of thin-film transistors (**TFTs**) [2, 11, 12]. For example, in [13], thin In–Si–O films were grown on a Si substrate using the co-sputtering method using In_2O_3 and SiO_2 targets, and the structural and optical properties of In–Si–O thin films were studied by inducing by means of increasing the amount of Si in the thin film transition from a nanocrystalline state to an amorphous one. In [14], it was found that the inclusion of SiO_2 in amorphous In_2O_3-based thin films suppresses the formation of unstable oxygen vacancies, thereby stabilizing the electrical properties, which made it possible to use the resulting thin film as a TFT channel.

Materials and Methods

Thin films $(In_2O_3/SiO_2)_{25}$ were obtained by ion beam sputtering of ceramic targets In_2O_3 and SiO_2 in an argon atmosphere with a purity of 99.998 % at a pressure $7 \cdot 10^{-4}$ Torr according to the procedure described in [15]. Targets were mounted on water-cooled copper substrates and placed in different sputtering positions in a vacuum chamber. In order to carry out layer-by-layer deposition, the substrate was moved from one sputtering position to another by rotating the substrate holder around the axis of the vacuum chamber. Deposition was carried out on substrates of monocrystalline silicon with a crystallographic orientation of (100) to study the structure and on substrates of glass to study the electrophysical properties. During the deposition process, the room temperature of the substrates was maintained, and the rotation rate of the substrate holder for $(In_2O_3/SiO_2)_{25}$ films was 0.13 rpm.

To obtain films with different thicknesses of In_2O_3 and SiO_2 layers, a screen with a V-shaped cut was mounted between the target and the substrate holder. The multilayer structure was deposited using pre-selected parameters of the sputtering process for each target. After applying the film from various sections, its thickness was measured using the MII – 4 interferometer. The thickness measurement points were fixed relative to the location of the substrate and the target. Knowing the depositing time and the time of one carousel revolution, the thickness of the film layer was calculated, obtained for one passage of the substrate by the substrate of the material deposition zone. In this way, the thickness of each multilayer structure layer was determined. As a result, structures were formed with a thickness of 140 to 200 nm, consisting of 25 In_2O_3/SiO_2 bilayers, with thickness values of 6.3 to 7.8 nm.

The structure and phase composition of the obtained films were studied by X-ray diffraction methods on a Bruker D2 Phaser diffractometer ($\lambda CuK\alpha 1 = 1.54$ Å) using the DIFFRAC.EVA 3.0 software with the ICDD PDF© database Release 2012.

The electrical resistance of $(In_2O_3/SiO_2)_{25}$ films was measured at various temperatures by the two-probe direct current method using a V7-78/1 AKIP© universal digital voltmeter. The relative error in measuring the electrical resistance of the studied thin films did not exceed 2 %.

Results and Discussion

XRD film measurement $(In_2O_3/SiO_2)_{25}$

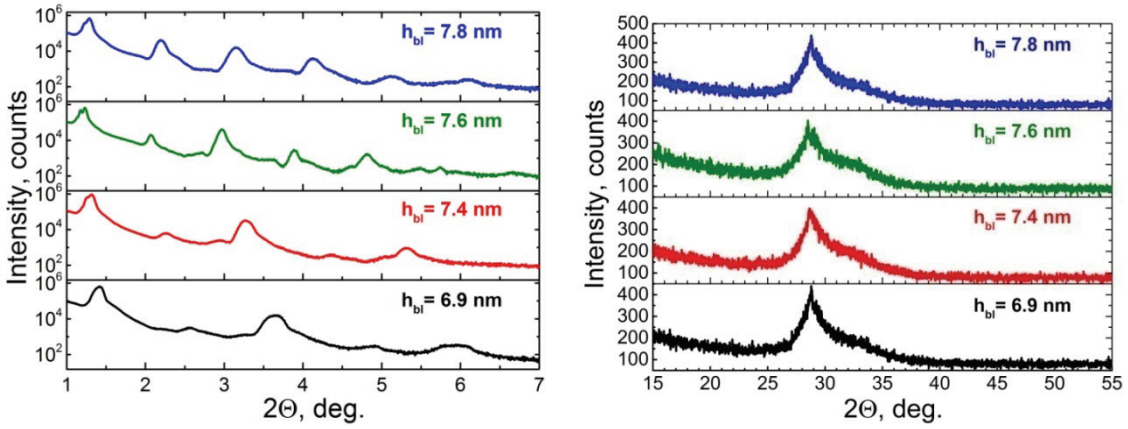
Certification of the structure and phase composition of the obtained samples of the system $(In_2O_3/SiO_2)_{25}$ was carried out by X-ray phase analysis. For all the samples studied, there are maxima in the X-ray diffraction patterns in the region of small Bragg angles (Fig. 1*a*), which indicates the formation of a layered structure.

The values of the multilayer structure period calculated by the Wulf–Braggs formula [16] are consistent with the results of estimates obtained using an optical interferometer:

$$n\lambda = 2d\sin\Theta, \qquad (1)$$

where Θ is Bragg angle; n is order of the diffraction maximum (in our case, $n = 1$); λ is x-ray wavelength.

The results of X-ray diffraction analysis (Fig. 1*b*) in the range of Bragg angles of 20–50° showed that all $(In_2O_3/SiO_2)_{25}$ films have an X-ray amorphous structure. The position of the broad diffraction



a) *b*)

Fig. 1. X-ray diffraction patterns from thin-film $(In_2O_3/SiO_2)_{25}$ heterostructures with different bilayer thicknesses (h_{bl})

maximum corresponds to $2\Theta \approx 29°$ and does not depend on the film thickness (h_{bl} bilayer thickness) in contrast to thin films of pure In_2O_3 obtained under similar conditions and having a polycrystalline structure (Fig. 2).

To analyze the structural changes that occur during heat treatment, thin films of In_2O_3 and $(In_2O_3/SiO_2)_{25}$ were annealed at a temperature of T_{ht} from 523 to 873 K for 30 minutes in vacuum at a residual pressure $P_{res} = 5 \cdot 10^{-2}$ Torr.

The results of X-ray phase analysis of the sample $(In_2O_3/SiO_2)_{25}$ with a bilayer thickness h_{bl} = 7.8 nm after such heat treatment are shown in Fig. 3.

The analysis of the X-ray diffraction patterns from thin films $(In_2O_3/SiO_2)_{25}$ in the region of small Bragg angles showed that after heat treatment at the studied temperatures the multilayer structure is preserved

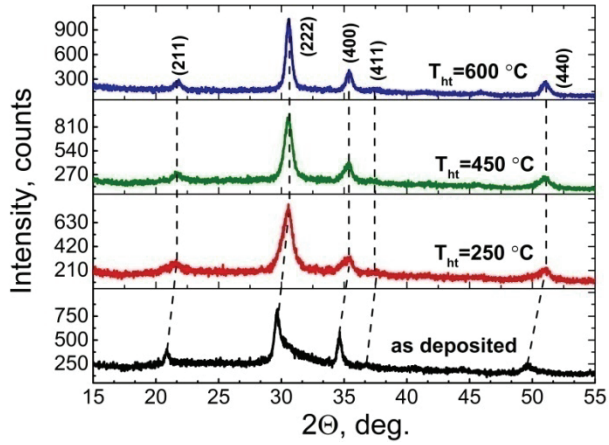
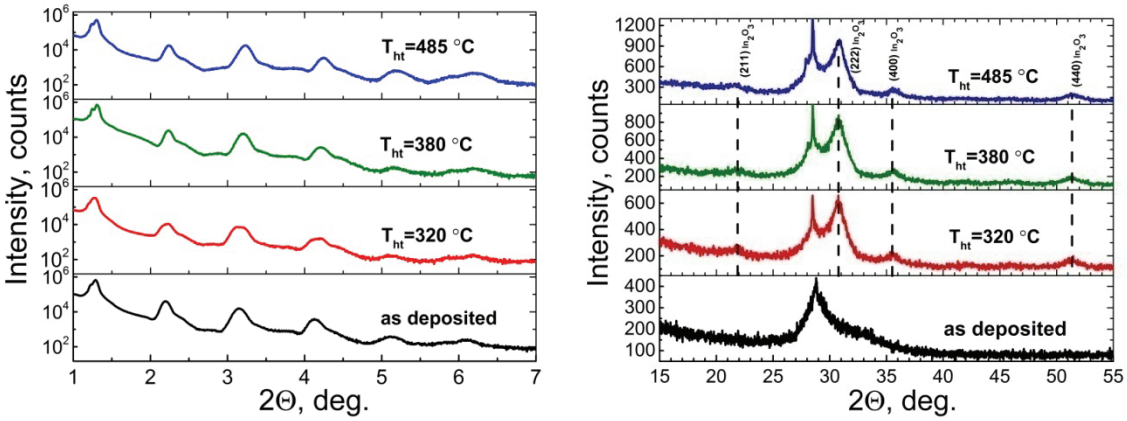


Fig. 2. X-ray diffraction patterns from a thin In_2O_3 film with a thickness h_{film}= 80 nm in the initial state and after heat treatment in vacuum for 30 min at different temperatures of T_{th}



a) *b*)

Fig. 3. X-ray diffraction patterns from thin-film $(In_2O_3/SiO_2)_{25}$ heterostructures with a bilayer thickness h_{bl} = 7.8 nm in the initial state and after heat treatment in vacuum $P_{res} = 5 \cdot 10^{-2}$ Torr for 30 minutes at various temperatures

(Fig. 3*a*). After heat treatment above 593 K, a crystalline In_2O_3 phase of cubic syngony with symmetry group Ia-3 is formed (Fig. 3*b*). However, in addition to the In_2O_3 crystalline phase, heat treatment even at 760 K does not lead to the complete disappearance of the amorphous phase (halo at $2\Theta \approx 28°$), which is probably SiO_2. Estimates of the average size of In_2O_3 crystallites in a multilayer structure $(In_2O_3/SiO_2)_{25}$ with a bilayer thickness $h_{bl} = 7.8$ nm were carried out according to the Scherrer formula [17]

$$D = \frac{0.89\lambda}{b\cos\Theta}, \qquad (2)$$

where λ is X-ray wavelength (1.54 Å for CuKα radiation); b is half-height reflex width; Θ is Bragg angle; D is the average crystal size given $D_{In_2O_3} \approx 7.5$ nm within the calculation error independent of the heat treatment temperature for $T_{ht} > 593$ K. The obtained values of the average In_2O_3 crystallite size do not exceed the bilayer thickness, which does not contradict the conclusion that the multilayer structure is preserved, made on the basis of the experimental results presented in Fig. 4*a*.

Electronic transport of the system $(In_2O_3/SiO_2)_{25}$ *in the temperature range from 77 to 300 K*

The relationship between the electrical resistivity and the thickness of the h_{bl} bilayer is shown in Fig. 4. The electrical resistivity of thin films $(In_2O_3/SiO_2)_{25}$ is more than an order of magnitude higher than that obtained for thin films of pure In_2O_3 of the same thickness ($\rho \sim 5 \cdot 10^{-4}$ Ohm·cm [18]), which can be related with scattering of charge carriers on the In_2O_3–SiO_2 interface. With an increase in h_{bl} from 6.3 to 7.8 nm, a monotonic decrease in ρ is observed from $8.89 \cdot 10^{-2}$ to $1.40 \cdot 10^{-2}$ Ohm·cm. This is explained by an increase in the thickness of the In_2O_3 conducting layer with a general increase in the bilayer thickness and a decrease in the contribution of charge carriers scattering at the In_2O_3–SiO_2 layer interfaces.

To establish the dominant mechanisms of electric transport in $(In_2O_3/SiO_2)_{25}$ films, the temperature relationships of the electrical resistivity $\rho(T)$ were studied in the temperature range from 77 to 300 K. The temperature relationships of the electrical resistance of thin $(In_2O_3/SiO_2)_{25}$ films with different bilayer thicknesses are presented in Fig. 5. The figure shows that these relationships have a negative temperature coefficient of resistance (**TCR**), which is characteristic of semiconductor materials. With increasing thickness of the h_{bl} bilayer, TCR in the studied temperature range decreases.

The analysis of the temperature dependences of the electrical resistivity of thin films $(In_2O_3/SiO_2)_{25}$ showed that in the temperature range from 77 to 150 K there is a linear section in the coordinates $\rho \sim \ln T$ (Fig. 6). It can be assumed that, in this case, just as for thin films of pure In_2O_3, in the temperature range 77–300 K, the electron transport is determined by the transition from transfer through delocalized states to weak localization of carriers and the appearance of quantum corrections to conductivity [19].

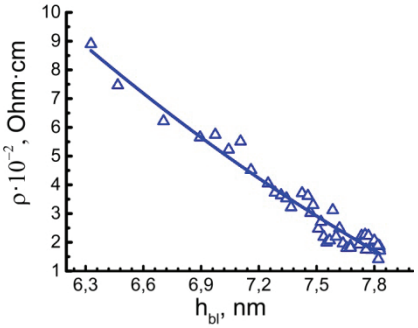


Fig. 4. Dependence of the electrical resistivity of thin-film heterostructures $(In_2O_3/SiO_2)_{25}$ on the h_{bl} bilayer thickness

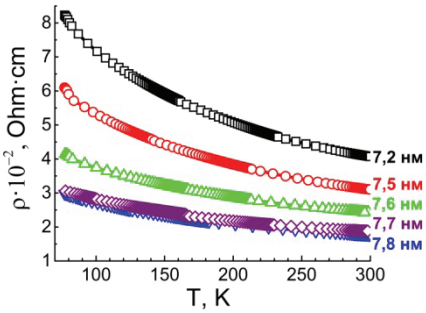


Fig. 5. Dependences of the electrical resistance of thin films $(In_2O_3/SiO_2)_{25}$ on different h_{bl} bilayer thicknesses as a function of temperature
(Thickness h_{bl} is indicated near the curves)

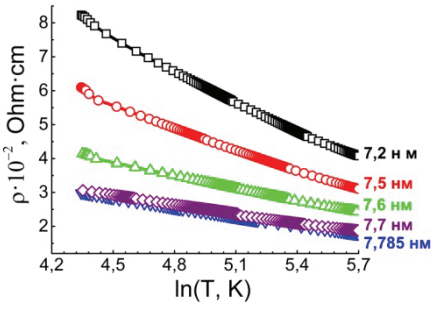


Fig. 6. Dependences of $R \sim f(\ln T)$ for $(In_2O_3/SiO_2)_{25}$ thin films with different bilayer thickness on temperature
(The h_{bl} bilayer thickness is indicated near the curves)

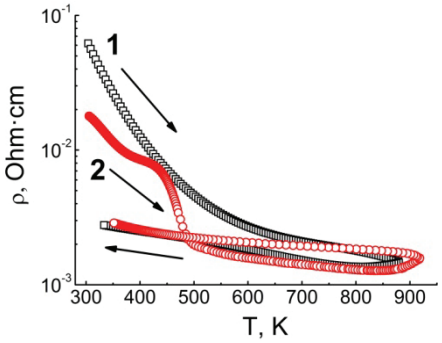


Fig. 7. Dependences of electrical resistivity on temperature measured in vacuum $P_{res} = 5 \cdot 10^{-2}$ Torr for thin films $(In_2O_3/SiO_2)_{25}$ with different h_{bl} bilayer thicknesses

The dependences of the electrical resistance of thin films $(In_2O_3/SiO_2)_{25}$ upon heating from room temperature to 600 K (Fig. 7) are characterized by a monotonically decreasing dependence $\rho(T)$, while the electrical resistivity decreases by more than 1–2 orders of magnitude. With an increase in the bilayer thickness, the portion of the most pronounced decrease in the electrical resistivity in the temperature range from 443 to 493 K (curve *2* in Fig. 6) begins to appear on the $\rho(T)$ dependences upon heating (which may indicate crystallization (recrystallization) of In_2O_3 amorphous layers). When heated above 493 K, the value of electrical resistivity changes slightly. The $\rho(T)$ dependences measured upon cooling are characterized by a negative TCR characteristic of semiconductor materials (Fig. 7).

In conclusion, it should be noted that during the heat treatment, the value of the electrical resistivity of the film decreases to $\rho \sim (2 \div 4) \cdot 10^{-3}$ Ohm·cm. The obtained $D_{In_2O_3}$ values for $(In_2O_3/SiO_2)_{25}$ multilayer structures after heat treatment remain lower than even those obtained for pure In_2O_3 films in the initial state (see Fig. 2), which indicates a high stability of the In_2O_3 nanostructured state modified by SiO_2 interlayers. This opens up possible prospects for the use of multilayer structures $(In_2O_3/SiO_2)_{25}$ as stable channels of thin-film transistors in transparent electronics.

Conclusion(s)

Multilayer thin films $(In_2O_3/SiO_2)_{25}$, consisting of layers of nanocrystalline In_2O_3 and interlayers of amorphous SiO_2 were synthesized by ion beam sputtering. The bilayer thickness of the obtained structures varied in the range from 5.5 to 8 nm. In the temperature range 77–300 K, the temperature dependences of the synthesized films electrical resistance were studied. It has been found that for $(In_2O_3/SiO_2)_{25}$ thin films in the temperature range studied, a logarithmic dependence between electrical resistance and temperature is observed, which is associated with the presence of weak localization of charge carriers and the influence of quantum corrections on conductivity.

The effect of heat treatment in vacuum at a residual pressure $P_{res} = 5 \cdot 10^{-2}$ Torr at various temperatures for 30 minutes on the structure and electrical properties of the synthesized films was studied. It has been found that the multilayer structure of thin films $(In_2O_3/SiO_2)_{25}$ is stable up to temperatures of 760 K, at which the average size of In_2O_3 crystallites does not exceed the equivalent bilayer thickness, and does not lead to the complete disappearance of the amorphous phase in the SiO_2 interlayer. Moreover, the electrical resistivity decreases to $\rho \sim 3 \cdot 10^{-3}$ Ohm·cm at room temperature, which allows to recommend the synthesized films $(In_2O_3/SiO_2)_{25}$ as stable channels of thin-film transistors in transparent electronics.

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