The Conductivity and Photoelectric Properties of β-Ga_2O_3 Thin Films

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Abstract—**Conductivity, photoconductivity and luminescence properties of β-Ga_2O_3 thin films deposited by high-frequency ion-plasma sputtering have been investigated depending on conditions and atmosphere of heat treatment. After annealing in a reducing atmosphere of hydrogen is a significant decrease in the resistivity of the films from the 10^{11} Ohm×cm for freshly prepared films to 10^6 Ohm×cm it was found. The analysis of the results was investigated. Irrespective of the composition of the atmosphere in annealing β-Ga_2O_3 thin films photoconductivity observed effect it was shown. Compare photoconductivity spectra with the spectra excitations of luminescence indicated that the photoconductivity of β-Ga_2O_3 thin films associated with band-band transitions with the creation of free charge carriers in the conduction band.**

Index Terms—**gallium oxide, thin films, conductivity, photoconductivity.**

I. Introduction

Recent studies have revealed a number of interesting properties of β–Ga_2O_3 thin films obtained by various methods [1]. Proceeding from this, the films based on β–Ga_2O_3 are widely used as thin-film materials for field effect transistors (FET) [2], gas sensors [3] and electrodes transparent in the UV region [4]. Depending on the method of obtaining and the dopant, such films are used as photoluminophors [5, 6], cathodoluminophors and electroluminophors [7, 8]. One of the important tasks for expanding the use of luminescent materials based on β–Ga_2O_3 is to increase the conductivity of these materials. One of the important tasks for expanding the use of luminescent materials based on β–Ga_2O_3 is to increase the conductivity of these materials. Several methods are used to change the conductivity of the β–Ga_2O_3 thin films, one of which is annealing in different atmospheres at high temperatures is used in this work.

II. Technique of the Experiment

Thin films of Ga_2O_3 were obtained by high-frequency (RF) ion-plasma sputtering on fused quartz substrates (ν-SiO_2). The thickness of thin films is 0.2 – 0.8 microns. After deposition the thin films were annealed in oxygen atmosphere or in argon atmosphere at 1000 – 1100 ° C, and also in hydrogen atmosphere at 600 – 650 ° C. X-ray diffraction studies have shown the presence of a polycrystalline structure, which differs depending on the method of heat treatment of the thin films (Fig. 1).

At annealing in oxygen atmosphere, the preferential orientation of the thin films is observed in the (400), (002), (111) and (512) planes. At the annealing in argon atmosphere the orientation (400), (002), (111), and (512) are also dominated, but there is a relative decrease in orientation in the (400) plane, an increase in the (111) plane, and an increase in orientation in the (113) plane. For films annealed in hydrogen atmosphere, an underdeveloped structure of the diffraction spectrum is observed, in which reflexes from the (400), (002), and (512) planes also predominate. The X-ray diffraction patterns showed no reflexes that do not correspond to β–Ga_2O_3, that is, no other phases were detected.

The conduction and photoconductivity currents in the range 200–800 nm were measured in an automated installation.

III. Results and Discussion

To change the electrical conductivity of thin-film phosphors of β–Ga_2O_3, they were annealed in an atmosphere of oxygen, argon and hydrogen. The temperature dependence of the electrical conductivity was measured and the energy of the thermal activation of the conductivity was determined for the thin films that investigated. Before annealing in a reducing atmosphere of hydrogen, the thin films had a large resistivity ($\rho > 10^{11}$ Ω×cm). To reduce the resistance of the β–Ga_2O_3 thin films, they were annealed in a reducing hydrogen atmosphere at 650 ° C. Such annealing leads to a significant reduction in the resistance to order of 10^6 Ω×cm (Fig. 2).

According to the results given in the review [9], gallium oxide of β–Ga_2O_3 can possess both dielectric properties and semiconductor properties. Such changes are caused by changes in the conditions for the synthesis of samples. In particular, the presence of oxygen vacancies and excessive gallium atoms in Ga_2O_3 leads to the formation of donors and, accordingly, n-type conductivity.

The question of the nature of electrical conductivity of thin films is more complex than in single-crystal samples. It is complicated by the fact that the thin films do not always have a perfect structure and can be amorphous or polycrystalline, contain inclusions of other phases. The obtaining of the

necessary and stable created properties of polycrystalline films is further complicated by the presence of inter-grain boundaries.

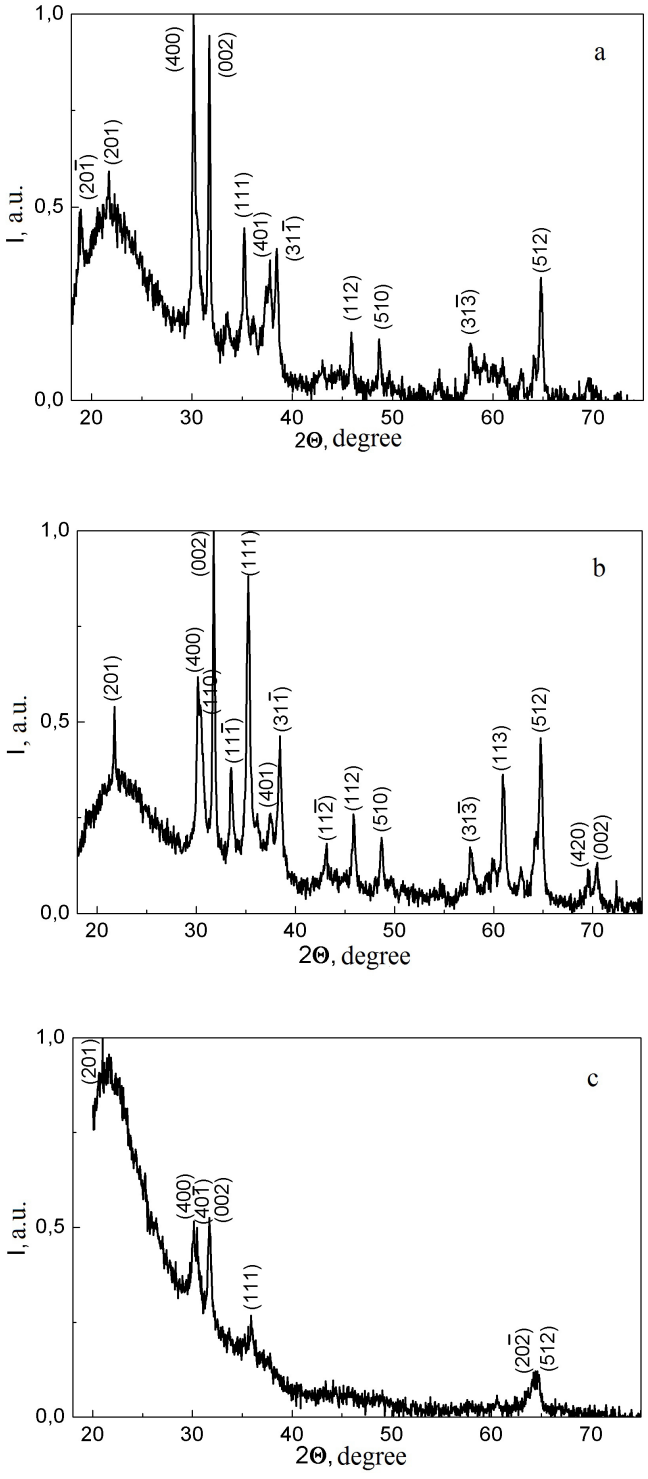

Figure. 1. X-ray diffraction (at CuK_α-radiation) of Ga_2O_3 thin films, obtained by RF ion-plasma sputtering, after annealing in oxygen atmosphere (a), argon (b) at 1000°C and in hydrogen atmosphere at 600°C (c).

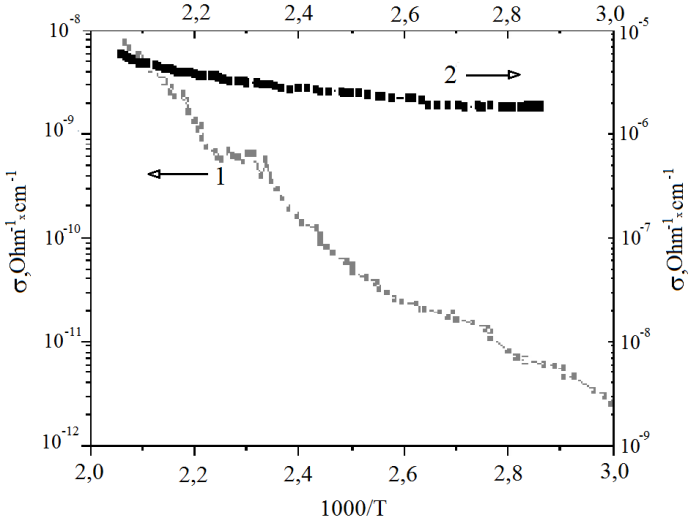

Figure 2. Temperature dependence of the electrical conductivity of β-Ga2O3 thin films to (1) and after (2) annealing in a flowing hydrogen atmosphere.

The electrically active centers are formed by the inter-grain boundaries in oxide and semiconductor thin films. Such centers can play the role of traps for electrons and holes, manifest themselves in recombination processes and thus affect the electrical conductivity and luminescence.

The annealing of thin films in a reducing atmosphere of hydrogen is accompanied by the creation of a large concentration of oxygen vacancies and excess gallium atoms [10–12]. As a result of this annealing, an increase in the conductivity of the thin films is observed.

Quasi-chemical reactions of creation of free charge carriers in Ga_2O_3 can be written using the notation [13] as follows:

$$Ga_2O_3 \Leftrightarrow 2Ga^x_{Ga} + 3V_o^{\bullet\bullet} + 1.5O_2 + 6e'$$

$$Ga_2O_3 \Leftrightarrow 2Ga^{\bullet\bullet\bullet}_i + 1.5O_2 + 6e'$$

$$Ga_2O_3 \Leftrightarrow 2Ga^x_{Ga} + 3V_o^{\bullet} + 1.5O_2 + 3e'$$

$$Ga_2O_3 \Leftrightarrow 2Ga^{\bullet\bullet}_i + 1.5O_2 + 4e'$$

$$Ga_2O_3 \Leftrightarrow 2Ga^{\bullet}_i + 1.5O_2 + 2e'$$

Depending on the dominant type of defect creation reaction, a different value of n in the equation $\sigma = kP_{O2}^{-1/n}$, which connects the conductivity and the oxygen partial pressure, should be expected.

The conducted studies of the conductivity of β–Ga_2O_3 thin films from the partial pressure of oxygen P_{O2} measured at different temperatures show that in high-resistance films, the conductivity is associated with the release of electrons from deep donor levels with the energy of occurrence of 0.84 eV that associated with oxygen vacancies. In addition to the deep donor centers created by oxygen vacancies in β–Ga_2O_3, there are small donor centers created by interstitial gallium or more

complex defects based on associates of gallium and oxygen vacancies and interstitial gallium. The depth of occurrence of such donor levels lies in the 0.15 eV region, that causes a higher conductivity.

The effect of photoconductivity is observed in thin films of β–Ga_2O_3 irrespective of the composition of the heat treatment atmosphere. The characteristic photoconductivity spectra of the resulting thin films are shown in Fig. 3. The obtained spectra show that the smallest photocurrent is observed in β–Ga_2O_3 thin films annealed in oxygen atmosphere, in which there is the least amount of oxygen vacancies. The largest photocurrent is characteristic for un-annealed films with an incompletely formed structure.

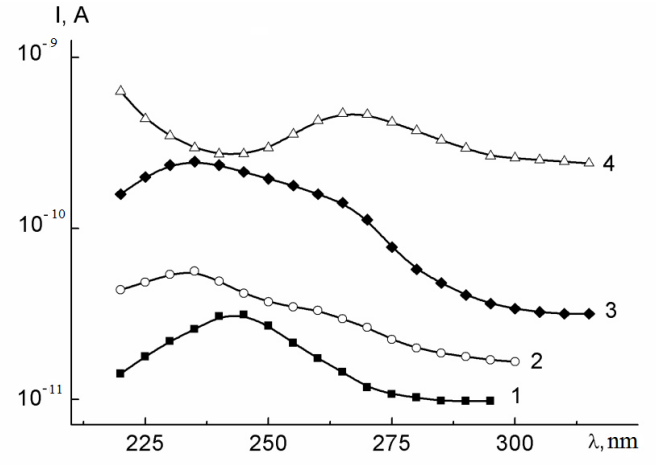

Figure 3. Photoconductivity spectra (T = 295 K) of β-Ga_2O_3 thin films after annealing in oxygen (1), argon (2), after reduction in hydrogen pre-annealed in argon (3) and un-annealed films (4).

As can be seen from Fig. 3, on the spectra of annealed β–Ga_2O_3 thin films irrespective of the annealing atmosphere, the two overlapping photoconductivity bands are observed in the spectral range 220 – 270 nm and the resulting spectrum represents a superposition of these bands.

The characteristic excitation spectra of the UV and blue bands of luminescence of β-Ga_2O_3 thin films, measured at 295 K, at the photoconductivity measurement temperature, are shown in Fig. 4. As can be seen from Fig. 4, irrespective of the presence of heat treatment for both types of thin films, the maximum excitation band for UV luminescence is in the region of 245 nm, and for blue luminescence, in the 250 nm region. Taking into account the presence of a spectral shift for the maximum excitation of these bands and the fact that they are excited in practically one spectral region of 230 – 270 nm, it can be assumed that the UV and blue bands of luminescence of β-Ga_2O_3 are most likely to have different nature, although the centers that responsible for these bands are interact very strongly. These two excitation bands are correlative well with two photoconductivity bands, which form the resulting photoconductivity spectrum. We also note that the photoconductivity spectrum of un-annealed β-Ga_2O_3 thin films correlates well with the photoexcitation spectra of UV and blue bands of luminescence of β-Ga_2O_3 ceramics (Fig. 4, c), from which of β-Ga_2O_3 thin films were deposited.

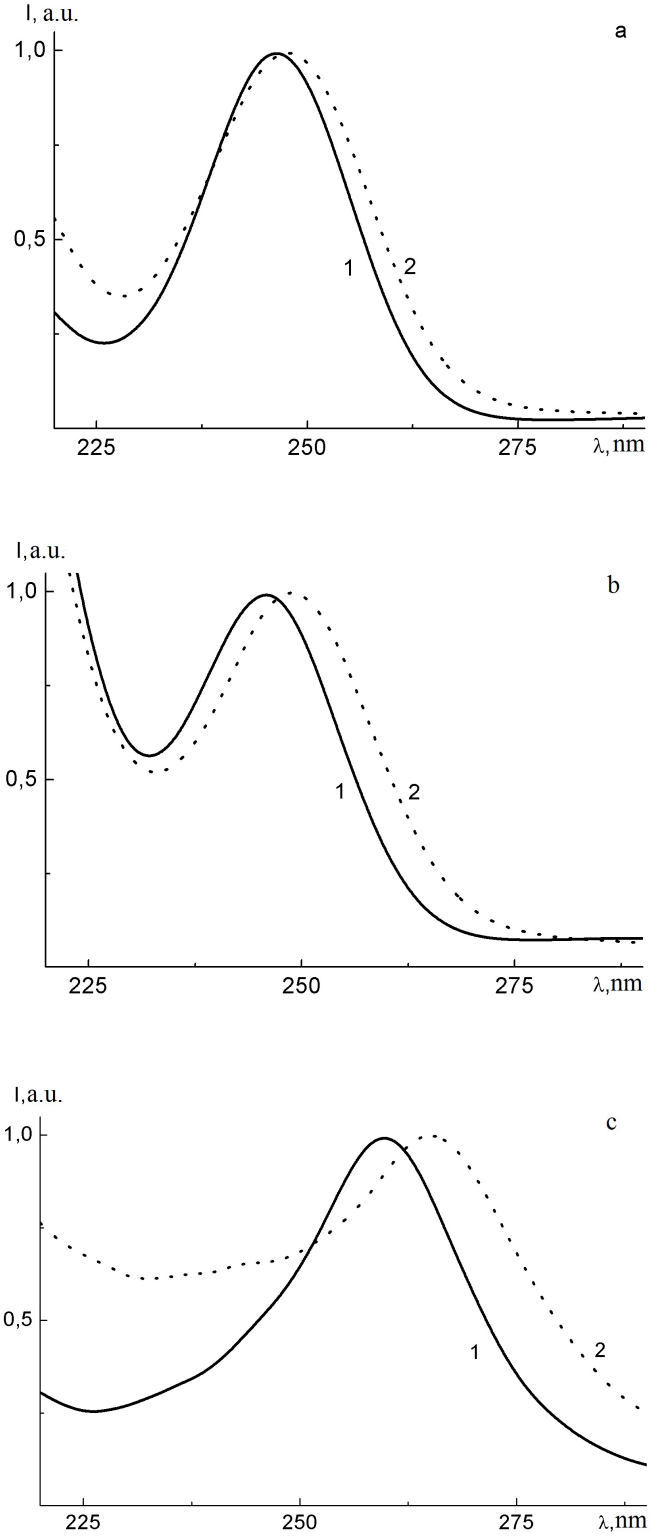

Figure 4. The excitation spectra of luminescence for the UV band of luminescence with a maximum at 397 nm (1) and the blue band of luminescence with a maximum at 449 nm (2) for the annealed of β–Ga_2O_3 thin films in the oxygen atmosphere (a), the un-annealed thin films (b) and ceramics (c); T = 295 K.

The results obtained show that the spectra of excitation of luminescence and photoconductivity of β–Ga_2O_3 thin films are in the same spectral region and correlate well with each other. A comparison of the spectra of photoconductivity, excitation of luminescence and the width of the band edge (E_g) shows that the photoconductivity in thin films of β–Ga_2O_3 is due to band-band transitions with the creation of free charge carriers in the conduction band. In accordance with the calculation of the electronic structure of β–Ga_2O_3 [14–16], such electronic transitions are realized from the 2p states of O that form the upper filled level of the valence band, to the bottom of the conduction band formed by the hybridized 2p states O and 4s-states of Ga.

IV. Conclusion

The carried out investigations showed that annealing of β-Ga_2O_3 thin films in the reducing atmosphere leads to a significant decrease in the resistance to value of 10^6 Ohm×cm relative to value of 10^{11} Ohm×cm for freshly prepared films. In high-resistance films, the conductivity is associated with the release of electrons from deep donor levels with the energy of occurrence of 0.84 eV and associated with oxygen vacancies, and for films reconstructed in hydrogen atmosphere, with the liberation of electrons from shallow donor levels with the energy of occurrence of 0.15 eV and associated with interstitial gallium atoms. Irrespective of the presence and composition of the annealing atmosphere, the photoconductivity effect is observed in β-Ga_2O_3 thin films. A comparison of the spectra of photoconductivity, excitation of luminescence and the width of the energy band shows that the photoconductivity in thin films of β-Ga_2O_3 is due to band-band transitions with the creation of free charge carriers in the conduction band.

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