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INFLUENCE OF THE OBTAINING CONDITIONS ON THE ELECTROCONDUCTIVITY OF Ga_2O_3 THIN FILMS

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The structure and electrical conductivity of β-Ga_2O_3 thin films obtained by the method of RF ion-plasma sputtering, depending on the composition of the thermal treatment atmosphere, were studied. It was found that β-Ga_2O_3 thin films annealed in an argon atmosphere and an oxygen atmosphere have a significant value of resistivity up to 10^{11} Ohm×cm, and after annealing in a reducing hydrogen atmosphere there is a significant decrease in the value of resistivity of the films up to 10^8 Ohm×cm. Studies of the temperature dependence of electrical conductivity in the temperature range from 300 to 450 K allowed determine the value of activation energy of thermal quenching of electrical conductivity due to donor centers that occur in the obtained films and the analysis of the received results is carried.

Key words: gallium oxide, thin films, electrical conductivity.

Introduction

The investigation of gallium oxide (Ga_2O_3), in particular its monoclinic modification, is of great interest to researchers due to the possibility of its application in power and radio frequency electronics. In recent years, devices with using β-Ga_2O_3 are widely used [1–3]. Gallium oxide as a luminescent material is also promising for use in optoelectronics to create displays, scintillators, UV detectors. The use of thin films based on β-Ga_2O_3 is promising for field-effect transistors (FET) [4] and gas sensors [5].

The electrical and optical properties of β–Ga_2O_3 thin films, as well as other metal oxide films, are determined by the methods they were obtained, the regimes of deposition and subsequent technological methods that are able to purposefully change the properties of thin layers of oxides. Depending on the method of obtaining and the dopant, β–Ga_2O_3 thin films can be used as photoluminophors [6, 7], cathodoluminophors or electroluminophors [8, 9].

One of the important tasks for expanding the possibilities of using luminescent films based on β-Ga_2O_3 is to increase their conductivity. Several methods are used to change the conductivity of β-Ga_2O_3 films, one of which – annealing in different atmospheres at high temperatures – is used in this work. In this work, thin films of β-Ga_2O_3 were investigated. Thin films are obtained by radio-frequency (RF) ion-plasma sputtering. The application of this method is considered as optimal for the deposition of semiconductor and dielectric thin films.

Experimental technique

Thin films of β-Ga_2O_3 with a thickness of 0.2–0.5 μm were obtained by RF ion-plasma sputtering on substrates of υ-SiO_2 fused quartz. RF sputtering was carried out in an atmosphere of argon in the system using the magnetic field of external solenoids for compression and additional ionization of the plasma column. After deposition of the films, the heat treatment in argon atmosphere at 1000–1100 °C, as well as in hydrogen atmosphere at 600–650 °C was held. The structure and phase composition of the obtained films by the method of X-ray diffraction analysis (Shimadzu XDR-600) was investigated.

The conduction currents in the temperature range 300–450 K were measured on an automated installation. An electrical voltage of 10 – 100 V was applied to two point contacts with a diameter of 1 mm, which were 1 mm spatially separated. When measuring the current flowing in β-Ga_2O_3 thin films, the main requirement is the use of ohmic not rectifier contacts, which don't create additional barriers at the interface. The ohmic contact to the investigated films is created by materials which, when at the directly shift, the injection of electrons into the film is provide and have an work function of ~ 4.5 eV. The polycrystalline carbon (aquadag) we use meets these requirements and is used in numerous publications in the study of diamond, garnet, spinel and other high-resistance oxygen-containing samples [10–13].

Results and discussion

X-ray diffraction studies for the obtained thin films of β-Ga_2O_3 showed the presence of a polycrystalline structure, which differs slightly depending on the method of heat treatment of the films. The characteristic diffraction patterns of the obtained films are shown in Fig. 1. Analysis of diffraction patterns shows that the structure of the obtained films corresponds to the monoclinic crystal structure of β-Ga_2O_3. We describe the structure of thin films in more detail in [14].

To study the change in the electrical conductivity of β–Ga_2O_3 thin film phosphors, their annealing was performed in an atmosphere of oxygen, argon, and hydrogen. For the studied films, the temperature dependence of the electrical conductivity was measured and the energy of thermal activation of the conductivity was determined from it. The obtained results showed that after sputtering the β–Ga_2O_3 films had the high resistivity ($\rho > 10^{11}$ Ohm× cm) and a rather high value of the thermal activation energy. The thermal annealing of β–Ga_2O_3 thin films in an oxygen atmosphere and an argon atmosphere did not significantly affect for the value of resistivity, measured at 295 K. However, at heated to 450 K, the value of resistivity decreased to 10^8 Ohm × cm. At annealing in an oxygen atmosphere, the energy of thermal activation of electrical conductivity for β–Ga_2O_3 thin films was 0.84 eV. At annealing in an argon atmosphere in the temperature range of 300 to 400 K, the energy of thermal activation of β–Ga_2O_3 films is 1.30 eV, at temperatures of 400 to 450 K is 0.40 eV.

To reduce the value of resistance of the obtained thin films, they were annealed in a reducing atmosphere of hydrogen at 650 °C. At annealing thin film in a hydrogen atmosphere, the value of resistivity decreases to the order of 10^8 Ohm×cm and the value of thermal activation of electrical conductivity for β – Ga_2O_3 thin films decreases to 0.15 eV (Fig. 2). According to [15], in β–Ga_2O_3 films samples, the resistivity is $\rho \approx 6 \times 10^{13}$ Ohm×cm. The characteristic values the energies of thermal activation of electrical conductivity for the obtained films are shown in table 1.

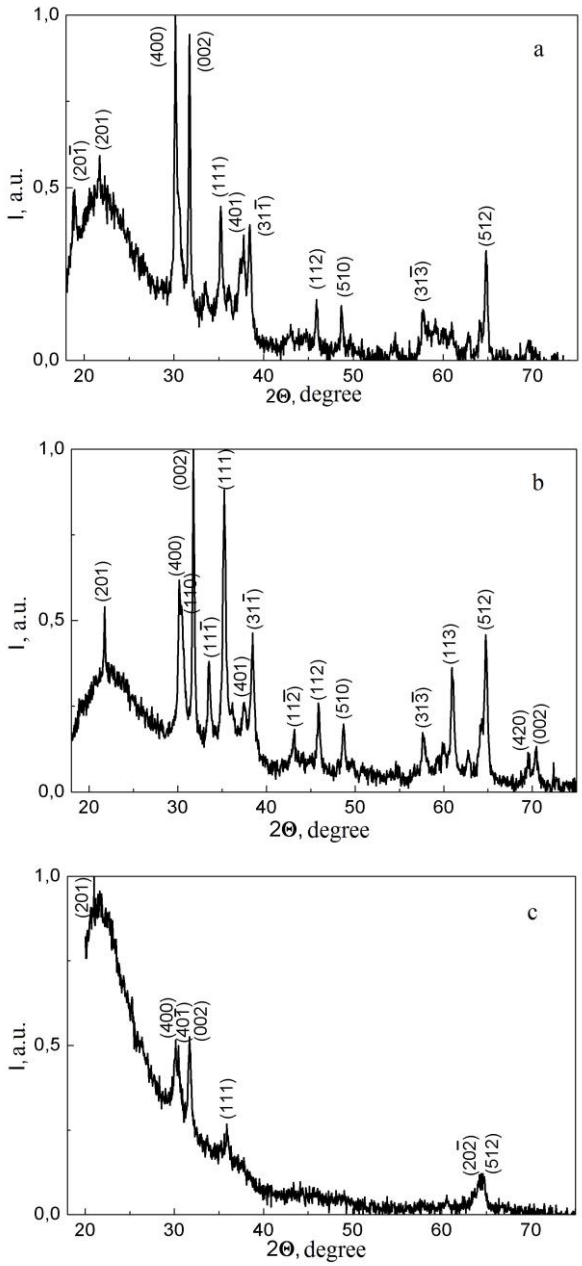

Fig. 1. The diffraction patterns (with CuK_α irradiation) of β-Ga_2O_3 thin films, obtained by RF ion-plasma sputtering, after thermal treatment in an atmosphere of oxygen (a), an atmosphere of argon at 1000 °C (b) and an atmosphere of hydrogen at 600°C (c)

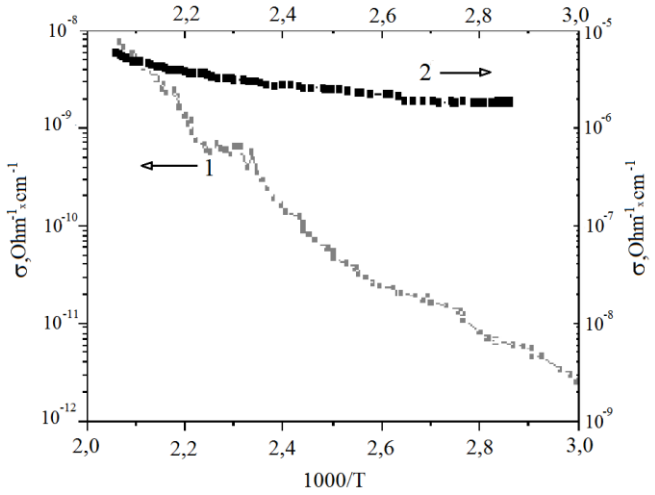

Fig. 2. The temperature dependence of the electrical conductivity of β–Ga_2O_3 films before (1) and after (2) annealing in a flowing hydrogen atmosphere

Table 1. The values of energy of thermal activation of electrical conductivity for β–Ga_2O_3 thin films

Atmosphere of annealing	Energy of thermal activation of electrical conductivity, eV
Oxygen	0.84
Argon	1.30 (300–400 K) 0.40 (400–450 K)
Hydrogen	0.15

Gallium oxide β–Ga_2O_3 can have both dielectric and semiconductor properties [16]. Such changes are due to changes in sample synthesis. The annealing of films in the reducing atmosphere of hydrogen is accompanied by the creation of a large concentration of oxygen vacancies and excess of gallium atoms [17, 18, 19]. Defects of both types manifest themselves as donors and lead to n-type conductivity [20]. As a result of such annealing, an increase in the conductivity of the studied films is observed.

Two different types of defects in gallium oxide can have donor properties –interstitial gallium atoms $Ga_i^{\bullet\bullet\bullet}$, $Ga_i^{\bullet\bullet}$, $Ga_i^{\bullet}$, Ga_i^{x} or vacancies $V_0^{\bullet\bullet}, V_0^{\bullet}, V_0^{x}$ in the oxygen sublattice [21]. The index "*x*" refers to neutral types of defects, and "•", "••", "•••" to single, double and triple positively ionized defects. These two types of defects describe the electrical properties of gallium oxide quite well [12].

Our research also showed that β-Ga_2O_3 films that were not subjected to pre-annealing in an atmosphere of oxygen or argon have a significantly higher conductivity after reductive annealing than films that underwent such pre-treatment at 1000 °C. This indicates that the creation of defects, associated with increased electrical conductivity, is much easier in films with incomplete structure formation. The observed effect is probably determined by the lower height of the energy barrier to create its own defects with an incompletely formed structure.

Conclusion

Studies have shown that annealing of β-Ga_2O_3 thin films in the reducing hydrogen atmosphere leads to a significant reduction in the value resistance to the value of resistivity of 10^8 Ohm×cm relative to 10^{11} Ohm×cm for films annealed in an oxidized oxygen atmosphere or in an inert argon atmosphere. In high-resistance films, the electrical conductivity is associated with the release of electrons from deep donor levels with energies of 0.84 eV for films annealed in oxygen atmosphere and 1.30 eV for films annealed in argon atmosphere and which are due to oxygen vacancies. In hydrogen-reduced β-Ga_2O_3 thin films, electrical conductivity is associated with the release of electrons from shallow donor levels with an energy of 0.15 eV due to interstitial gallium atoms.

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ВПЛИВ УМОВ ОДЕРЖАННЯ НА ЕЛЕКТРОПРОВІДНІСТЬ ТОНКИХ ПЛІВОК Ga_2O_3

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Досліджено структуру та електропровідність тонких плівок β-Ga_2O_3, одержаних методом високочастотного іонно-плазмового розпилення, залежно від складу атмосфери термообробки.

ВЧ розпилення проводилось в атмосфері аргону на підкладках із плавленого кварцу. Аналіз дифрактограм показує, що структура отриманих плівок відповідає моноклінній кристалічній структурі β-Ga_2O_3. Встановлено, що тонкі плівки β-Ga_2O_3, відпалені в атмосфері аргону та кисню при 1000–1100°С, володіють значним питомим опором – до 10^{11} Ом×см, а після відпалу у відновній атмосфері водню спостерігається зниження питомого опору плівок до 10^8 Ом×см. Дослідження температурної залежності електропровідності в області температур 300 – 450 К дозволили визначити енергію активації температурного гасіння електропровідності за рахунок донорних центрів, що виникають в одержаних плівках, та проведено аналіз отриманих результатів. Енергія термічної активації електропровідності при відпалі в атмосфері кисню для плівок β–Ga_2O_3 становить 0,84 еВ. При відпалі в атмосфері аргону в температурній області 300 – 400 К енергія термічної активації плівок β–Ga_2O_3 становить 1.30 еВ, при температурах 400 – 450 К – 0.40 еВ. Відпал у атмосфері водню призводить до суттєвого зменшення опору і зменшення енергії термічної активації електропровідності до 0.15 еВ. При цьому у високоомних плівках електропровідність пов'язується зі звільненням електронів з глибоких донорних рівнів з енергіями залягання 0.84 еВ для плівок, відпалених у кисні та 1.30еВ, для плівок, відпалених у аргоні, і які зумовлені кисневими вакансіями. У відновлених у водні тонких плівках β-Ga_2O_3 електропровідність пов'язується зі звільненням електронів з мілких донорних рівнів з енергією залягання 0.15 еВ, які зумовлені міжвузловими атомами галію.

Ключові слова: оксид галію, тонкі плівки, електропровідність.

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