

PACS numbers: 61.72.jn, 68.55.jd, 73.50.Gr, 73.61.-r, 78.60.Kn, 81.15.-z

Electrical Conductivity of Pure and Cr³⁺-Doped β -Ga₂O₃ Thin Films

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The electrical conductivity of pure and Cr³⁺-doped β -Ga₂O₃ thin films is studied. As found, the thin films of β -Ga₂O₃ and β -Ga₂O₃:Cr³⁺ annealed in an oxygen atmosphere have a low conductivity of the order of 10⁻¹⁰ Ohm⁻¹·cm⁻¹. The conductivity of such films is associated with the release of electrons from deep donor levels due to oxygen vacancies. At annealing within the reducing atmosphere, the specific conductivity of β -Ga₂O₃ thin films increases to 10⁻³ Ohm⁻¹·cm⁻¹ and is associated with shallow donor levels due to interstitial gallium atoms. At annealing within the reducing atmosphere, the specific conductivity of β -Ga₂O₃:Cr³⁺ thin films increases to 10⁻⁸ Ohm⁻¹·cm⁻¹ and related with deep donor levels due to chromium-impurity ions in the Cr²⁺ state. The relationship between the luminescence and the conductivity in β -Ga₂O₃:Cr³⁺ thin films is analyzed. As shown, by changing the thermal-treatment conditions for the β -Ga₂O₃:Cr thin films, it is possible to change the concentration of chromium-impurity ions in the Cr²⁺ and Cr³⁺ states and, thus, to control the electrical conductivity and luminescence.

Досліджено електропровідність чистих та активованих йонами Cr³⁺ тонких плівок β -Ga₂O₃. Встановлено, що відпалені у кисневій атмосфері тонкі плівки β -Ga₂O₃ та β -Ga₂O₃:Cr³⁺ мають низьку питому електропровідність порядку 10⁻¹⁰ Ом⁻¹·см⁻¹. Провідність таких плівок пов'язується зі звільненням електронів із глибоких донорних рівнів, зумовлених Оксигеновими вакансіями. За відпалу у відновній атмосфері питома

провідність тонких плівок $\beta\text{-Ga}_2\text{O}_3$ зростає до 10^{-3} $\text{Ом}^{-1}\cdot\text{см}^{-1}$ та пов'язується з мілкими донорними рівнями, зумовленими міжвузловими атомами Галію. За відпалу у відновній атмосфері питома провідність тонких плівок $\beta\text{-Ga}_2\text{O}_3\text{:Cr}^{3+}$ зростає до 10^{-8} $\text{Ом}^{-1}\cdot\text{см}^{-1}$ і пов'язується з глибокими донорними рівнями, зумовленими домішковими йонами Хрому у стані Cr^{2+} . Проведено аналізу взаємозв'язку між люмінесценцією та провідністю в тонких плівках $\beta\text{-Ga}_2\text{O}_3\text{:Cr}^{3+}$. Показано, що, змінюючи умови термооброблення тонких плівок $\beta\text{-Ga}_2\text{O}_3\text{:Cr}$, можна змінювати концентрацію домішкових йонів Хрому у станах Cr^{2+} й Cr^{3+} і тим самим контролювати електропровідність і люмінесценцію.

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

Ключові слова: оксид Галію, тонкі плівки, активатор, провідність.

(Received 12 April, 2022)

1. INTRODUCTION

The great interest of researchers in the study of thin films of metal-oxide materials is due to the possibility of their use in modern instrumentation and optoelectronics. Among such materials, the $\beta\text{-Ga}_2\text{O}_3$ films occupy an important place; they have a number of interesting properties, which are determined by ways and methods of fabrication. Depending on the method of obtaining and the type of dopant, the pure and doped thin films of $\beta\text{-Ga}_2\text{O}_3$ are used as phosphors with photoluminescence [1, 2], cathodoluminescence or electroluminescence [3, 4], as transparent conductive electrodes [5].

The practical use of $\beta\text{-Ga}_2\text{O}_3$ thin films stimulates widely the investigation of alloying impurities for the formation of levels of capture and recombination of charge carriers in the band gap that affects significantly on the electrophysical properties of these films. Such impurities include an impurity of Cr^{3+} , the ionic radius of which is close to the ionic radius of the cation, and it causes large intensity of the intracentre emission [6, 7]. Several methods are used to change the electrical conductivity of thin films based on $\beta\text{-Ga}_2\text{O}_3$, one of which, namely, annealing in different atmospheres at high temperatures, is used in this work. In this work, thin films of $\beta\text{-Ga}_2\text{O}_3$ and $\beta\text{-Ga}_2\text{O}_3\text{:Cr}^{3+}$ are 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 [8].

2. EXPERIMENTAL TECHNIQUE

Thin films of $\beta\text{-Ga}_2\text{O}_3$ and $\beta\text{-Ga}_2\text{O}_3\text{:Cr}^{3+}$ with a thickness of 0.2–1.0

μm were obtained by RF ion-plasma sputtering on substrates of ν -SiO₂ fused quartz. After deposition of films, they were heat-treated in oxygen atmosphere at 1000–1100°C, as well as, they were reduced in hydrogen at 600–650°C. X-ray diffraction studies showed the presence of a polycrystalline structure, which differs slightly, depending on the chemical composition and method of thermal treatment of films. We give the typical diffraction patterns and their analysis on the example of β -Ga₂O₃ thin films earlier in Ref. [9]. It is also shown that the films are formed from nanocrystallites, the size of which is determined by the conditions of fabrication. In particular, after annealing within the oxygen atmosphere, the average diameter of the crystallites is of 47 nm, and after annealing within hydrogen atmosphere, it is of 35 nm [9].

Gallium oxide of 99.99% was used as a raw material for the deposition of thin films. An alloying impurity in the form of Cr₂O₃ oxide with a concentration of 0.01–0.1 wt.% was added to β -Ga₂O₃ in the manufacture of targets for film deposition.

The conduction currents in the temperature range 300–450 K were measured on an automated installation. An electric voltage of 10–100 V was applied to two point contacts with a diameter of 1 mm, which were separated at a distance of 1 mm. When measuring the current flowing in the studied thin films, the main requirement is the use of ohmic non-rectifying contacts, which do not create additional barriers at the interface. The ohmic contact to the investigated films is created by materials, when, at the direct shift, the injection of electrons into the film is provided, having a work output of $\cong 4.5$ eV. The polycrystalline carbon (aquadag), which we use, meets these requirements and has been reported in numerous publications about its use in the study of diamond, garnet and other high-resistance oxygen-containing samples [10–14], including β -Ga₂O₃ [15–17].

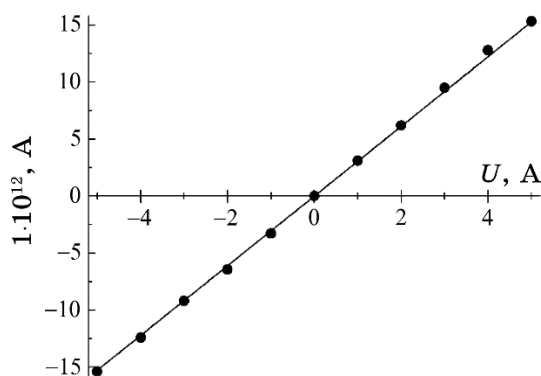


Fig. 1. Voltage–current characteristic of β -Ga₂O₃ thin films.

Our investigation on the AutoLab impedance spectrometer showed that the voltage–current characteristics of the studied films are described by a linear dependence in the range of electric fields up to $5 \cdot 10^3$ V/m. The characteristic behaviour of the voltage–current characteristic for the β -Ga₂O₃ thin film is shown in Fig. 1.

3. RESULTS AND DISCUSSION

Our researches have shown that thermal treatment of β -Ga₂O₃ thin film within the reducing hydrogen atmosphere leads to an increase in electrical conductivity. The obtained results are in good agreement with previous our studies [9] and show that the thermal activation energy of electrical conductivity decreases to 0.1 eV (Fig. 2). Subsequent annealing of low-ohmic β -Ga₂O₃ thin films within the oxygen atmosphere leads to a decrease of electrical conductivity that indicates the relationship of the donor levels with oxygen loss.

In general, donors' properties in β -Ga₂O₃-based thin films can be possessed by two types of intrinsic defects of the crystal lattice, namely, interstitial gallium ions or oxygen vacancies, which have captured 'excess electrons' [18]. The results of studies of the dependence of electrical conductivity on the partial pressure of oxygen, carried out in [19], make it possible to determine the degree of ionization of defects. From the obtained results, it follows that the electrical conductivity of β -Ga₂O₃ is due to the release of electrons from oxygen vacancies V_o^x and single ionized atoms of interstitial gallium Ga_i , which play the role of donor centres.

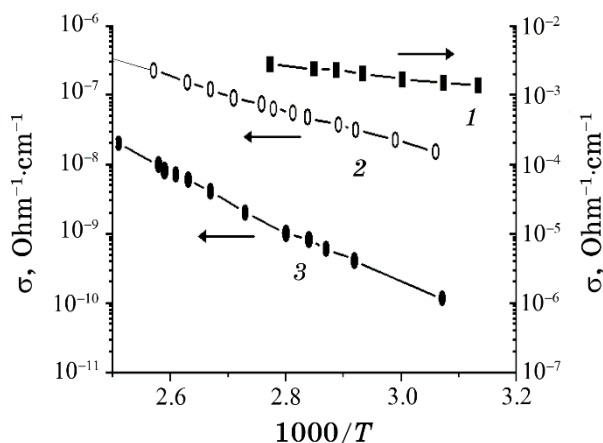


Fig. 2. The temperature dependence of specific conductivity for thin films of (1, 3) β -Ga₂O₃ and (2) β -Ga₂O₃:Cr annealed within the hydrogen (1, 2) and oxygen (3) atmospheres.

Taking into account that, in alkali-halide crystals, the anionic vacancy creates deep levels of electron capture (up to 2 eV) and also based on the results of determining the deep levels of oxygen vacancy of V_o in oxides of ZnO and MgO [20], it should be expected that oxygen vacancies in β -Ga₂O₃ create deep levels of electron capture too. Based on previous studies [9], it can be suggested that the electrical conductivity of high-resistivity β -Ga₂O₃ thin films is due to the release of electrons from the V_o^x centres created by oxygen vacancy (activation energy of 0.84 eV) into the conduction band. In addition to deep donor levels, β -Ga₂O₃ also contains shallow levels with activation energies in the region up to 0.15 eV [9]. The value of activation energy decreases with increasing degree of recovery.

The shallow donor levels are associated with interstitial gallium atoms. According to the data of [21–23], the interstitial gallium atom must be once ionized Ga_i. This shallow donor model well agrees with the hypothesis that green luminescence in β -Ga₂O₃ is related to intracentre transitions in mercury-like Ga⁺ centres. As the temperature increases, the donor centre Ga_i is ionized that leads to the observed temperature attenuation of the emission. At the same time, it follows from luminescent studies that the concentration of green luminescence centres depends weakly on the degree of oxygen defects [24–26].

Given the possibilities of wide application in luminescent technology of luminescent impurity-doped β -Ga₂O₃ thin films, we investigated the effect of Cr³⁺-impurity centres on the electrical conductivity of these films.

According to Ref. [7], the red photoluminescence and several thermally-stimulated luminescence (TSL) bands with maxima near 265, 285, 300, 320, 354 and 385 K are observed for the β -Ga₂O₃:Cr³⁺ single crystals. Our investigation of TSL in thin films of β -Ga₂O₃:Cr³⁺ showed the presence of only one band of TSL with a maximum in the region of 290 K (Fig. 3). Probably, other possible bands of TSL due to the low intensity of the emission could not be detected.

To estimate the depth of occurrence of the detected capture centre, the estimated ratio according to Urbach's formula $E_T = 25kT_m$ was used [27], where value of $E_T \approx 0.62$ eV was established. The obtained value correlates well with the results in Ref. [7] for single-crystal samples.

The investigation shows that, after thermal treatment within the hydrogen atmosphere, the resistivity of β -Ga₂O₃:Cr³⁺ thin films decreases from 10¹¹ Ohm·cm to 10⁶–10⁸ Ohm·cm with value of the thermal-activation energy of 0.6 eV (Fig. 2). After such annealing, the quenching of red luminescence is observed, and TSL is absent. The red photoluminescence of β -Ga₂O₃:Cr³⁺ thin films increases after

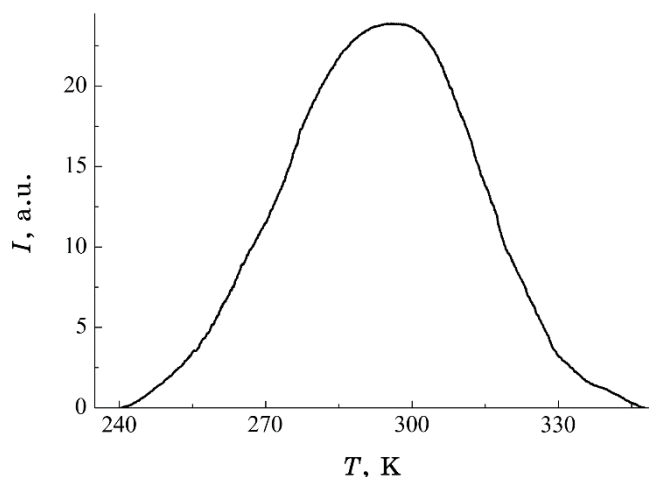


Fig. 3. The TSL curves for the $\beta\text{-Ga}_2\text{O}_3\text{:Cr}^{3+}$ thin films annealed within the oxygen atmosphere at registration in the red region of the spectrum ($\lambda > 650$ nm).

thermal treatment within the oxygen atmosphere or, according to Ref. [28], after the introduction of divalent impurities (Mg or Zn), which form deeper levels of capture than Cr^{3+} ions.

Based on the obtained data, the mechanism of changes in the conductivity of $\beta\text{-Ga}_2\text{O}_3$ thin films in the presence of a luminescent impurity Cr^{3+} can be explained as follows. The shallow donor levels with a depth of occurrence near 0.1 eV for the thin films of $\beta\text{-Ga}_2\text{O}_3\text{:Cr}^{3+}$ after thermal treatment in a reducing atmosphere are formed. However, the electrons from these levels are recaptured by deep centres; because of this, the photoluminescence intensity of Cr^{3+} ions decreases and TSL becomes absent. The conductivity is determined by the thermal transition of electrons from the Cr^{2+} level (the energy depth of 0.62 eV) to the conduction band. As a result, the electrical resistivity of Cr^{3+} -doped $\beta\text{-Ga}_2\text{O}_3$ thin films decreases less than that of undoped thin films, and the value of activation energy is higher than that of undoped thin films and is of 0.6 eV (compared to 0.15 eV in Ref. [9]). After the next thermal treatment within the oxygen atmosphere, in undoped and Cr^{3+} -doped $\beta\text{-Ga}_2\text{O}_3$ thin films, the value of resistivity increases to $10^9\text{--}10^{10}$ Ohm-cm, and the value of activation energy increases to 0.84 eV. In addition, the increasing intensity of red photoluminescence in thin films of $\beta\text{-Ga}_2\text{O}_3\text{:Cr}^{3+}$ is observed.

To describe the relationship between luminescence and conductivity in $\beta\text{-Ga}_2\text{O}_3\text{:Cr}^{3+}$ thin films, it should be taken into account that the introduction of Cr^{3+} impurities into the $\beta\text{-Ga}_2\text{O}_3$ crystal lattice

leads to the formation in the band gap of an electron capture level (Cr²⁺) with an energy depth of 0.62 eV. Since the concentration of introduced impurities is of the order of 0.01–0.1 wt.%, the concentration of the created levels of electron capture is of the order of 10¹⁸–10¹⁹ cm⁻³ that is of the same order or greater than the possible concentration of oxygen vacancies. The introduction of deep levels of electron capture into the β -Ga₂O₃ crystal lattice leads to the fact that ‘free’ electrons are relocalized from shallow levels with an energy of the order of 0.1 eV to deeper levels with an energy of 0.62 eV (in states with minimum energy). Such localization of electrons on the deeper levels leads to an increase in the value of activation energy of electrical conductivity and, as a consequence, to an increase in the value of resistance of the thin films.

The value of the activation energy of electrical conductivity of β -Ga₂O₃:Cr³⁺ thin films is quite close to the depth of occurrence of the donor level Cr²⁺, as obtained from TSL data. Note that the capture of ‘free’ electrons by chromium ions is equivalent to its recharging to the Cr²⁺ state. Because of such capture, the concentration of impurity ions in the trivalent state decreases that manifests itself in a decrease in the luminescence efficiency of Cr³⁺ ions. The subsequent reannealing of β -Ga₂O₃ thin films within the oxygen atmosphere leads to a decrease in the concentration of oxygen vacancies as well as free electrons, which are captured by the capture centres. The electrical conductivity, close to the stoichiometry of β -Ga₂O₃ thin films, is controlled by the deep centre V_o^x ($E = 0.84$ eV). Given that, the depth of the Cr²⁺ level ($E = 0.62$ eV) is less than V_o^x , in the case of high-ohms films, the recharging of impurities does not occur because the electrons are trapped at deeper levels. Thus, if changing the thermal-treatment conditions of β -Ga₂O₃:Cr³⁺ thin films, it is possible to change purposefully the concentration of impurity chromium ions in the divalent and trivalent states. The luminescence efficiency of Cr³⁺-impurity ion varies more than ten times.

4. CONCLUSIONS

The investigation have shown that annealing in the reducing atmosphere of pure and Cr³⁺-activated β -Ga₂O₃ thin films leads to a significant increase of the specific conductivity from 10⁻¹⁰ Ohm⁻¹.cm⁻¹ to 10⁻³ Ohm⁻¹.cm⁻¹ for pure β -Ga₂O₃ thin films and up to 10⁻⁸ Ohm⁻¹.cm⁻¹ for thin films of β -Ga₂O₃:Cr³⁺. In high-ohms films, the conductivity is associated with the release of electrons from deep donor levels with the energy value of 0.84 eV that is associated with oxygen vacancies. At annealing in a reducing atmosphere, the conductivity of β -Ga₂O₃ thin films is associated with the release of electrons from shallow donor levels with the energy value of 0.15

eV that is associated with interstitial gallium atoms. At annealing of β -Ga₂O₃:Cr³⁺ thin films in a reducing atmosphere, the conductivity is associated with the release of electrons from deep levels with the energy value of 0.62 eV that is associated with impurity chromium ions in the Cr²⁺ state.

It was found that, at changing the thermal-treatment conditions for the β -Ga₂O₃:Cr³⁺ thin films, it is possible to change the concentration of impurity chromium ions in the Cr²⁺ and Cr³⁺ states in a controlled manner and, thus, to control the electrical conductivity and luminescence.

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