Photoconductivity of Thin β-Ga$_2$O$_3$ and β-Ga$_2$O$_3$:Cr^{3+} Films

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The presence of photoconductivity in thin films of β-Ga$_2$O$_3$ and β-Ga$_2$O$_3$:Cr^{3+} obtained by radio-frequency (RF) ion-plasma sputtering after heat treatment in air has been established. The obtained photoconductivity spectra are analysed, and it is shown that the photoconductivity in pure thin β-Ga$_2$O$_3$ films is due to intrinsic photoconductivity because of the band−gap electronic transitions. In thin β-Ga$_2$O$_3$:Cr^{3+} films, in addition to this photoconductivity band, there are also three photoconductivity bands observed due to electronic transitions within the Cr^{3+} activator ion. At the same time, all three excited levels fall into the conduction band and lead to the appearance of *U*-, *Y*-, and *V*-bands of photoconductivity.

Встановлено наявність фотопровідности у тонких плівках β-Ga$_2$O$_3$ та β-Ga$_2$O$_3$:Cr^{3+}, яких було одержано методом високочастотного (ВЧ) йонно-плазмового розпорошення після термооброблення на повітрі. Проаналізовано одержані спектри фотопровідности та показано, що у чистих тонких плівках β-Ga$_2$O$_3$ фотопровідність зумовлено власною фотопровідністю за рахунок зона-зонних електронних переходів. У тонких плівках β-Ga$_2$O$_3$:Cr^{3+}, крім даної смуги фотопровідности, спостерігаються ще три смуги фотопровідности, зумовлені електронними переходами в межах йона-активатора Cr^{3+}. Всі три збуджені рівні попадають у зону провідности та приводять до появи *U*-, *Y*- і *V*-смуг фотопровідности.

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

Ключові слова: оксид Ґалію, тонкі плівки, активатор, фотопровідність.

1. INTRODUCTION

Recent studies have revealed a number of interesting properties of pure and activated thin films of β-Ga_2O_3 obtained by various methods. Based on this, films based on β-Ga_2O_3 are widely used as thin-film materials for field-effect transistors [1], gas sensors [2], and UV-transparent electrodes [3]. Depending on the preparation method and the dopant, such films are used as photoluminophors [4, 5], cathodoluminophors, and electroluminophors [6, 7]. In this regard, chromium impurity Cr^{3+}, whose ionic radius is close to the ionic radius of the cation and causes a high brightness of intracentre luminescence, belongs to promising activators in β-Ga_2O_3 films [8−10].

In the general case, the optical and electrical properties of thin β-Ga_2O_3 and β-Ga_2O_3:Cr^{3+} films are determined by the preparation methods, deposition modes, and subsequent technological methods. For the deposition of films based on β-Ga_2O_3, a whole set of methods is used, from thermal evaporation to low-temperature chemical ones, such as hydrothermal, glycothermal, or electrochemical oxidation [11−14]. As a result, due to varying degrees of perfection, such films differ in optical, luminescent, and electrical properties. In this regard, the photoelectric properties of thin β-Ga_2O_3 and β-Ga_2O_3:Cr^{3+} films obtained by radio-frequency (RF) ion-plasma sputtering, the use of which leads to the deposition of the most homogeneous semi-conductor and dielectric films, are studied. Such studies expand the scope of application of thin β-Ga_2O_3 and β-Ga_2O_3:Cr^{3+} films, in particular, in photoelectronics, and allow a broader investigation of the electronic processes occurring in these films.

2. EXPERIMENTAL TECHNIQUE

Thin films of β-Ga_2O_3 and β-Ga_2O_3:Cr^{3+} with a thickness of 0.2−1.0 μm were obtained by RF ion-plasma sputtering on substrates of fused quartz υ-SiO_2. After the films were deposited, they were heat-treated in air at 1000−1100°C. Studies of x-beam diffraction have shown the presence of a polycrystalline structure of the resulting films. In more detail, the characteristic diffraction patterns and their analysis on the example of β-Ga_2O_3 films were presented earlier in Ref. [16]. It was also shown there that, upon annealing in an oxygen-containing atmosphere, films are formed from nanocrystals with an average diameter of 47 nm.

Gallium oxide of 99.99% purity (high purity) was used as a raw material for thin-film deposition. The trace impurity in the form of Cr_2O_3 oxide with a concentration of 0.05 wt.% was added to β-Ga_2O_3 in the manufacture of targets for film deposition.

The photoconductivity of thin β-Ga_2O_3 films with a change in the
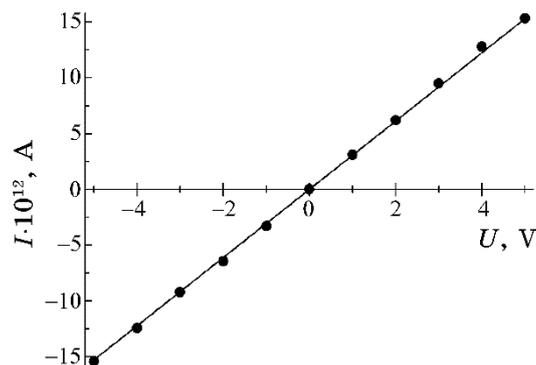
Fig. 1. Current−voltage characteristic of thin β-Ga$_2$O$_3$ films.

spectral composition of the exciting light with a constant number of quanta incident on the film (isoquantum spectral sensitivity) was measured on an automated setup mounted on the base of 'СФ-4А' spectrophotometer. Normalization in the spectral region 220−650 nm (5.6−1.9 eV) was carried out according to yellow lumogen, the luminescence quantum yield of which does not depend on the energy of exciting photons. An electrical voltage of 10−100 V was applied to two point contacts of 1 mm in diameter, which were at a distance of 1 mm. When measuring the electric current flowing in the films under study, the main requirement is the use of non-rectifying ohmic contacts, which do not create additional barriers at the interface. The ohmic contact for the films under study is created by materials, which, when forward biased, provide the injection of electrons into the film and have a work function of $\cong 4.5$ eV. The polycrystalline carbon (aquadag) we use meets these requirements, and numerous publications report on its use in the study of diamond, garnet, and other high-resistivity oxygen-containing samples [17−20], including β-Ga$_2$O$_3$ [21−23].

Our studies on the AutoLab impedance spectrometer showed that the current−voltage 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 current−voltage characteristics for a thin film of β-Ga$_2$O$_3$ is shown in Fig. 1.

3. RESULTS AND DISCUSSION

Our previous studies [24] show that, after heat treatment in hydrogen, the resistivity of thin films of β-Ga$_2$O$_3$:Cr³⁺ decreases and, in parallel, quenching of red luminescence is observed. Red photoluminescence in β-Ga$_2$O$_3$:Cr³⁺ films increases after treatment in an ox-

ygen-containing atmosphere. Considering the prospects for the practical use of β-Ga$_2$O$_3$ as a red phosphor [8–10], we studied the photoconductivity of pure and Cr^{3+}-activated thin β-Ga$_2$O$_3$ films annealed in air.

The characteristic photoconductivity spectra of thin films of β-Ga$_2$O$_3$, which are pure and activated by Cr^{3+} ions, are shown in Fig. 2. As can be seen from the results presented, the spectra differ significantly from each other. The photoconductivity spectrum of thin β-Ga$_2$O$_3$:Cr^{3+} films has a much more complex structure, and the photoconductivity current is more than two orders of magnitude higher than the photoconductivity current in pure β-Ga$_2$O$_3$ films. In this case, both photoconductivity spectra clearly show a photoconductivity band with a maximum in the region of about 245 nm (5.05 eV), which correlates well with the UV photoexcitation and blue luminescence bands in pure β-Ga$_2$O$_3$ films [23, 25]. Because the band gap in thin films of β-Ga$_2$O$_3$ after annealing in an oxygen atmosphere is of 4.60 eV [26], the excitation of the luminescence and photoconductivity bands occurs in the region of band–band transitions with the formation of free charge carriers in the band. As a result, intrinsic optical generation and, correspondingly, intrinsic photoconductivity arise. According to calculations of the electronic energy structure of β-Ga$_2$O$_3$ [27–29], such electronic transitions occur from the 2p states of O, which form the upper filled level of the valence band, to the bottom of the conduction band, which is formed by hybridized 2p states of O and 4s states of Ga.

Taking into account that there are no other photoconductivity bands in thin films of β-Ga$_2$O$_3$, and in thin films of β-Ga$_2$O$_3$:Cr^{3+}, a number of bands are observed in the spectral region of 280–650 nm, it is logical to relate these photoconductivity bands to Cr^{3+}.
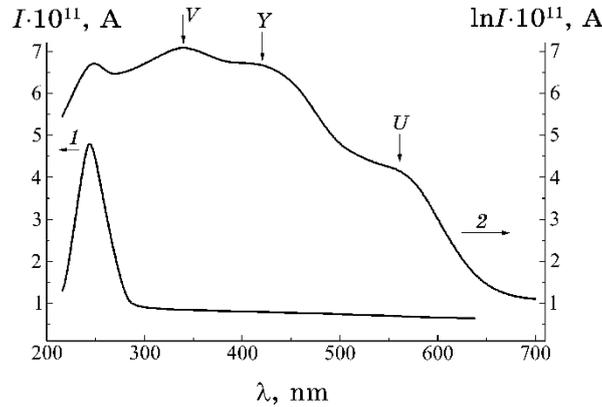
Fig. 2. Photoconductivity spectra of thin β-Ga$_2$O$_3$ (*1*) and β-Ga$_2$O$_3$:Cr^{3+} (*2*) films; $T = 295$ K.

To analyse the relationship between the photoluminescent properties and photoconductivity in thin β-Ga$_2$O$_3$:Cr^{3+} films, one should proceed from the fact that the introduction of Cr^{3+} impurities into the β-Ga$_2$O$_3$ crystal lattice leads to the formation of an electron capture level (Cr^{2+}) in the band gap with an energy depth of 0.62 eV [24]. This energy corresponds to the ground term of the ion to the Cr^{3+} orbital singlet $^4A_2$ (t_2^3). Electronic transitions $^4A_2 \rightarrow {}^4T_2$ (t_2^2 $^3T_1$, e) (U), $^4A_2 \rightarrow {}^4T_1$ (t_2^2 $^3T_1$, e) (Y) and $^4A_2 \rightarrow {}^4T_1$ (t_2, e^2 $^3A_2$) (V) within the Cr^{3+} ion give three broad bands in the absorption spectra: U-, Y-, and V-bands, respectively [30]. Based on this, the characteristic three long-wavelength photoconductivity bands can be associated with the U-band (with a maximum in the region of 600 nm), Y-band (with a maximum in the region of 440 nm), and V-band (with a maximum in the region of 330 nm) (Fig. 2). In this case, all three excited levels fall into the conduction band. Most likely, these levels do not mix with the levels of the allowed zone, but a potential barrier separates them from it. Due to such a barrier, electrons tunnel from these levels both into the conduction band and into back. The equality of these fluxes leads to the establishment of an equilibrium concentration of Cr^{3+} ions.

4. CONCLUSIONS

The conducted studies show that, in thin films of β-Ga$_2$O$_3$, which are pure and activated by Cr^{3+} ions, after heat treatment in air, the effect of photoconductivity is observed. Comparison of the photoconductivity spectra shows that the photoconductivity spectra in thin films of β-Ga$_2$O$_3$:Cr^{3+} have a more developed structure and, along with the band of intrinsic photoconductivity due to band−band transitions (in the region of about 245 nm), contain three broad bands due to electronic transitions, namely, U-, Y- and V-bands. In this case, all three excited levels fall into the conduction band.

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