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Origin of Point Defects in β-Ga_2O_3 Single Crystals Doped with Mg^{2+} Ions

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Optical absorption and photoconductivity investigations of nominal pure and Mg^{2+} doped β-Ga_2O_3 single crystals have been carried out. Additional bands in the UV (3.6–4.6 eV) and near-IR (0.4–1.2 eV) spectral regions were found in optical absorption and photoconductivity spectra. A correlation between Mg^{2+} doping, annealing in oxygen atmosphere as well as optical absorption and photoconductivity bands were established in gallium oxide. Electronic transitions from shallow traps and F-centers were observed in the IR spectral region (0.4–1.2 eV). Absorption and photoconductivity in the UV region are related to deep acceptor levels created by native defects and impurities.

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1. Introduction

Gallium oxide (β-Ga_2O_3) is a promising conductive material for use in optical devices that work in the ultraviolet (UV) spectral region as well as in devices for power electronics due to the large band gap ($\approx$ 4.8 eV) and the possibility of controlled doping by donor impurities. Recently, metal–semiconductor field-effect transistor (MESFETs) [1, 2], metal–oxide–semiconductor field-effect transistor (MOSFETs) [1, 3] and the Schottky barrier diode (SBDs) [4, 5] based on β-Ga_2O_3 were produced. Already the first tests showed that the characteristics of devices based on β-Ga_2O_3 for applications in power electronics can be better than Si and other types of wide-gap semiconductors such as SiC and GaN [3].

However, the successful use of β-Ga_2O_3 as a material for devices of power electronics, optoelectronics in the UV spectral region and other applications is hampered by the small amount of papers devoted to studying the fundamental properties of β-Ga_2O_3, including the role of impurities and host defects in donor and acceptor levels creating, which play a crucial role in the charge transfer.

The optical absorption spectra of β-Ga_2O_3 single crystals for the first time were investigated in [6–8]. It was established that the location of the fundamental absorption edge depends on the relative orientation of the electric vector $\boldsymbol{E}$ of the light wave and the crystallographic axes of the crystal. Moreover, photoconductivity was observed at the crystal excitation in the absorption edge range. However, the detailed studies of the optical absorption and photoconductivity of β-Ga_2O_3 single crystals in the range of crystal transparency and the information about the relationship of impurities and intrinsic defects with local levels created in the band gap are limited in the literature.

The aim of this work is to reveal the nature of point defects that arise in gallium oxide with the introduction of Mg^{2+} impurities and deviation from the stoichiometry in the growing process and thermal treatment of β-Ga_2O_3 crystals.

2. Experimental

β-Ga_2O_3 single crystals were grown by the zone floating technique with radiation heating from gallium oxide (99.99% purity). Some samples after growing were annealed in an oxygen atmosphere to decrease the concentration of oxygen vacancies. The investigations were carried out on undoped as-grown crystals of β-Ga_2O_3, crystals annealed at 1450 °C for 50 h in an oxygen atmosphere, and crystals doped with Mg^{2+} impurity. The concentration of Mg^{2+} ions in the charge for crystals growing was 0.1 at.%. Undoped as-grown β-Ga_2O_3 crystals have a blue coloration. β-Ga_2O_3 crystals annealed in an oxygen atmosphere as well as doped with Mg^{2+} impurity are colorless.

A set of the samples with a thickness from 40 μm to 5 mm was used to study the optical absorption in a wide range of absorption coefficient value. Samples were received in the form of plane-parallel plates by cleavage of the single crystal on the main plane (100). The investigation of the optical absorption and photoconductivity were carried out in the polarized light. The direction of the light beam coincides with the perpendicular to the plane (100). Electric vector $\boldsymbol{E}$ of light wave was oriented parallel or perpendicular to the axis $\boldsymbol{b}$ of the crystal.

Absorption spectra in the ultraviolet (UV) and visible spectral region were recorded with the spectrophotometer "Specord M40" as well as in the IR spectral region — with "Specord M60" and "Specord 75IR". Photoconductivity spectra were measured using the spectrophotometer SF-4A. Indium films on the (100) plane were used

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as electrodes with ohmic contact. The photocurrents, which were of the order of 10^{-10} to 10^{-14} A, were detected with an electrometer. Light from a Xenon lamp was used to the photoconductivity excitation. Photoconductivity spectra were corrected for the spectral distribution of the lamp. All measurements were carried out at 90 and 290 K.

3. Results

Figure 1 shows the absorption spectrum of β-Ga_2O_3 single crystal in the UV spectral region at room temperature for orientation $\boldsymbol{E} \parallel \boldsymbol{b}$. The absorption coefficient for all samples is growing rapidly and consistent with the formula for direct allowed transitions at the energy of light quanta more than 4.8 eV (curve 1). The experimental points are well approximated by a straight line. The intersection of this line with the abscissa gives the value of band gap $E_g = 4.98$ eV at 290 K for β-Ga_2O_3 single crystal. The activation with Mg^{2+} impurity and high-temperature annealing in an oxygen atmosphere do not affect the position of the fundamental absorption edge.

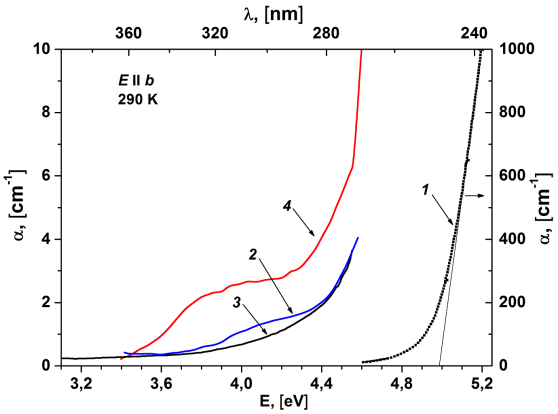

Fig. 1. Absorption spectra of β-Ga_2O_3 single crystals in the UV spectral region at room temperature for $\boldsymbol{E}\|\boldsymbol{b}$ orientation: 1 — fundamental absorption (scale right), 2 — as-grown crystal, 3 — crystal annealed in an oxygen atmosphere, 4 — β-Ga_2O_3: Mg^{2+} crystal.

The absorption curves are somewhat different for samples with different prehistory in the range before the absorption edge at the energy values $h\nu < 4.6$ eV. There is a broad absorption band in the energy range 3.2-4.6 eV with a shoulder at 3.8–4.2 eV in the undoped as-grown β-Ga_2O_3 crystal (curve 2). Annealing of β-Ga_2O_3 crystal in an oxygen atmosphere (curve 3) leads to a slight decrease of the broad band absorption at 3.2–4.6 eV.

Significant changes are observed in the absorption spectrum of β-Ga_2O_3 crystals activated with Mg^{2+} ions in 3.2–4.6 eV range (curve 4). There is a general increase of the absorption coefficient at about 2–3 times in the 3.5–4.6 eV range for the β-Ga_2O_3: Mg^{2+} crystals. The band with a maximum near 3.8 eV and absorption near 4.5–4.6 eV imposed on the absorption edge can be

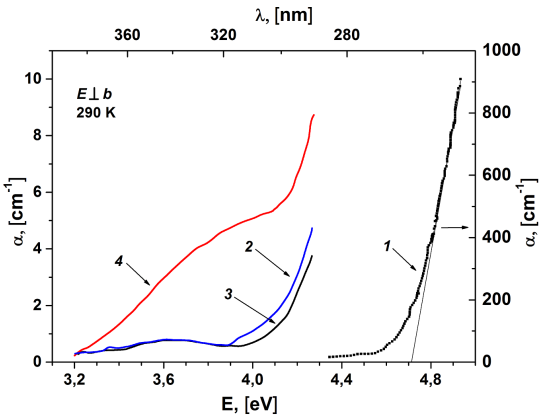

Fig. 2. Absorption spectra of β-Ga_2O_3 single crystals in the UV spectral region at room temperature for $\boldsymbol{E}\perp\boldsymbol{b}$ orientation: 1 — fundamental absorption (scale right), 2 — as-grown crystal, 3 — crystal annealed in an oxygen atmosphere, 4 — β-Ga_2O_3: Mg^{2+} crystal.

distinguished on the background of mentioned above absorption.

The rapid increase of the absorption coefficient begins at much less energy ($h\nu > 4.5$ eV) for $\boldsymbol{E}\perp\boldsymbol{b}$ orientation (Fig. 2). The calculated value of the band gap is 4.72 eV for $\boldsymbol{E}\perp\boldsymbol{b}$ at 290 K.

Broad absorption band in the energy range 3.2–4.3 eV was also observed in undoped as-grown crystals (curve 2) for $\boldsymbol{E}\perp\boldsymbol{b}$ orientation. Absorption in this region decreased slightly (curve 3) after annealing in an atmosphere of oxygen. Additional broad absorption band with a maximum near 3.8 eV (curve 4) is dominated in β-Ga_2O_3 crystals doped with Mg^{2+} impurity in the energy range 3.2–4.3 eV, similarly as in the case, of $\boldsymbol{E}\|\boldsymbol{b}$. Because the absorption edge for orientation $\boldsymbol{E}\perp\boldsymbol{b}$ starts at lower energies, this band is superimposed on the absorption edge and leads to increase of the absorption near 4.1 eV at about twice. The short-wavelength absorption band at 4.4–4.6 eV observed for the orientation $\boldsymbol{E}\|\boldsymbol{b}$ is much stronger superimposed on the absorption edge for the orientation $\boldsymbol{E}\perp\boldsymbol{b}$ and it is more difficult separated from the background of the absorption edge. Cooling of the β-Ga_2O_3 crystals to 90 K leads to a short-wavelength shift of the fundamental absorption edge. The energy value of interband transitions increases and is equal to 5.08 eV in the case $\boldsymbol{E}\|\boldsymbol{b}$ and 4.9 eV for $\boldsymbol{E}\perp\boldsymbol{b}$.

The same absorption bands in 3.2–4.6 eV range exist in as-grown, annealed in an oxygen atmosphere and activated with Mg^{2+} impurity of β-Ga_2O_3 crystals at 90 K, analogical as at room temperature. At the same time, the absorption coefficient increases 2–3 times compared to room temperature in the crystals activated with Mg^{2+} at low temperatures.

Figure 3 shows the absorption spectra of β-Ga_2O_3 single crystals in IR spectral region 0.4–2.0 eV range. It should be noted that there is no significant difference in the IR absorption spectra for $\boldsymbol{E}\|\boldsymbol{b}$ and $\boldsymbol{E}\perp\boldsymbol{b}$ orienta-

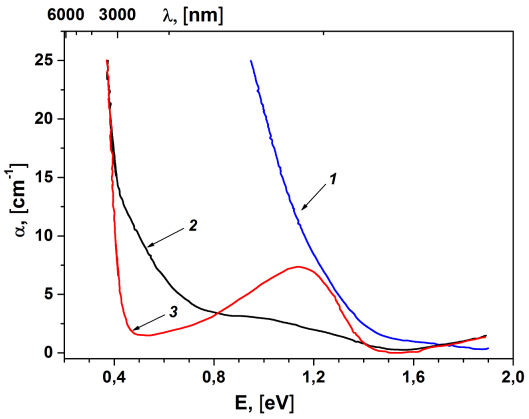

Fig. 3. Absorption spectra of β-Ga_2O_3 single crystals in the IR spectral region at room temperature: 1 — as-grown light-blue crystal, 2 — crystal annealed in an oxygen atmosphere, 3 — β-Ga_2O_3: Mg^{2+} crystal.

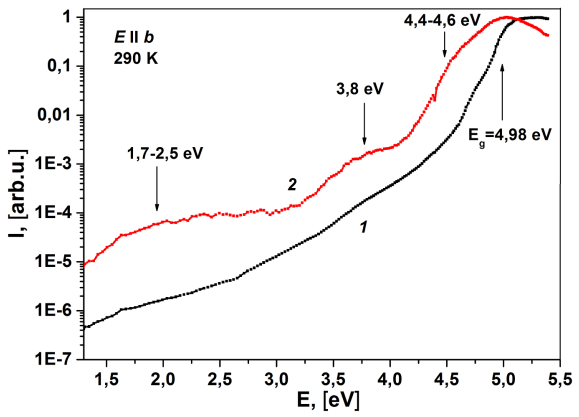

Fig. 4. Photoconductivity spectra of β-Ga_2O_3 single crystals at 290 K for $\boldsymbol{E}\|\boldsymbol{b}$ orientation: 1 — crystal annealed in an oxygen atmosphere, 2 — β-Ga_2O_3: Mg^{2+} crystal.

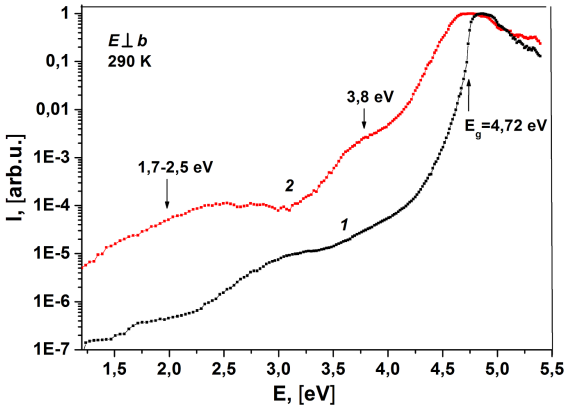

Fig. 5. Photoconductivity spectra of β-Ga_2O_3 single crystals at 290 K for $\boldsymbol{E}\perp\boldsymbol{b}$ orientation: 1 — crystal annealed in an oxygen atmosphere, 2 — β-Ga_2O_3: Mg^{2+} crystal.

tions. A significant increase of the absorption coefficient in as-grown crystals start at energies $h\nu < 1.4$ eV, moreover at $h\nu < 1$ eV absorption coefficient reaches 20 cm^{-1} (curve 1).

The blue coloration of the β-Ga_2O_3 crystal disappear and the long-wavelength border of crystals transparency is shifted to the infrared region after annealing in an oxygen atmosphere (curve 2). Low-intensity absorption bands in the form of shoulders close to 1.2 and 0.5–0.6 eV can be seen in annealed crystals in the energy range 0.4–1.4 eV. IR absorption maximum is observed in the vicinity of 1.2 eV as well as a strong increase of absorption begin at energies less than 0.4 eV in β-Ga_2O_3 crystals activated with magnesium.

As-grown undoped gallium oxide crystals are of low resistance. The negligibly small photoconductivity was revealed on the background of dark current at the excitation in the fundamental absorption edge and its long-wavelength side. However, it was not possible to register the spectral dependence of photocurrent.

Annealing of undoped β-Ga_2O_3 crystal in the oxygen atmosphere leads to an increase in resistivity of 10^3–10^4 times, making possible to register the photoconductivity spectra at 290 and 90 K.

Normalized spectra of photoconductivity are presented in logarithmic scale since the photocurrent changes by 5–7 orders of magnitude under the illumination light energy changing from 1 eV to 5.5 eV. The arrow in Fig. 4 indicates the position of the fundamental absorption edge of β-Ga_2O_3 crystals. The broad band of 5.1 eV for $\boldsymbol{E}\|\boldsymbol{b}$ (Fig. 4) and 4.8 eV for $\boldsymbol{E}\perp\boldsymbol{b}$ (Fig. 5) is dominant at 290 K in the excitation spectrum of photoconductivity of β-Ga_2O_3 crystal annealed in an oxygen atmosphere (curve 1). The position of this photoconductivity band is in good correlation with the position of the fundamental absorption edge and corresponds to the direct band-to-band transitions. Weak photoconductivity band strongly overlapped to the band-to-band transitions can be identified in the energy range 4.4–4.8 eV before the absorption edge for the crystals annealed in oxygen.

The main peak of 5.1 eV for $\boldsymbol{E}\|\boldsymbol{b}$ (Fig. 4) and 4.8 eV for $\boldsymbol{E}\perp\boldsymbol{b}$ (Fig. 5) is also observed in the range band-to-band transitions in the photoconductivity excitation spectra of β-Ga_2O_3 single crystals doped with magnesium impurity (curve 2). The photocurrent output increases in the region of 4.4–4.8 eV before the edge with the introduction of Mg^{2+} ions in comparison with the undoped as-grown samples. Besides, the relative intensity of the 3.8 eV band increases and weak photoconductivity appears at the excitation in the red spectral range 1.5–2.5 eV in the β-Ga_2O_3 samples doped with Mg^{2+} ions. It should be noted that the intensity of long-wavelength photoconductivity band also increases at the temperature decrease.

Cooling of β-Ga_2O_3 crystals to the temperature of liquid nitrogen increases the yield of photocurrent. Moreover, the short-wavelength shift of photoconductivity is

observed for a peak at 5.1 eV for $\boldsymbol{E}\|\boldsymbol{b}$ and 4.8 eV for $\boldsymbol{E}\perp\boldsymbol{b}$ that responsible for the band-to-band transitions. The positions of photoconductivity broad bands before edge do not change at cooling and coincide quite well with optical absorption bands that arise in β-Ga_2O_3 single crystals.

4. Discussion

It is known that in crystals grown in the oxygen-depleted atmosphere a significant number of defects is formed. Thermal treatment of β-Ga_2O_3 crystals in an oxygen atmosphere or doping with divalent magnesium impurity lead to a changing in the concentration of host defects and their charge states. These defects are responsible for local levels in the band gap of β-Ga_2O_3 that appear in optical absorption and photoconductivity spectra. The relative intensity of optical absorption and photoconductivity bands depends on thermal treatment and doping. It shows the correlation between these bands and host defects that are responsible for local levels in the band gap.

The simplest host point defects, that can occur at β-Ga_2O_3 single crystals growth, are positively charged oxygen vacancies $V_O^{\bullet\bullet}$, negatively charged gallium vacancies V_{Ga}''', and interstitial cations of $Ga_i^{\bullet\bullet\bullet}$ and O_i''. Whereas, in most of the cases, the growth process proceeds in the oxygen-depleted atmosphere, the probability of creation of interstitial oxygen defects (O_i'') in obtained samples is small. Decrease of the β-Ga_2O_3 density after annealing in vacuum [9] and during annealing in an oxygen atmosphere at T>1400 °C [10] can indicate that the formation of point defects in the gallium oxide takes place mainly on the Schottky mechanism. A high number of oxygen and gallium vacancies are creating during growth process at high temperatures. Formation of large concentrations of these vacancies is also contributed by dissociation of Ga_2O_3 to Ga_2O and O_2 and further sublimation of Ga_2O from a melt. The point defects are very mobile at growth temperatures. Threefold charged cationic vacancies due to high electrostatic interaction with oxygen vacancies create more stable associates of $(V_{Ga}V_O)^{1-}$ type and thus partly compensate the free positive electric charges. These negatively charged vacancies associates can behave as acceptors in undoped gallium oxide crystals. Due to the existence of two different crystallographically non-equivalent positions of gallium and three positions of oxygen, there is the probable formation of associates with different energies, which leads to expansion of levels in the sub-band, and it can be observed in the broad absorption and photoconductivity bands. The confirmation of the prevailing creation of vacancy associates can be found in the results obtained by authors of the paper [10] who have investigated β-Ga_2O_3 single crystals by high-resolution transmission electron microscopy (HRTEM). The point defects are clearly seen in the HRTEM image given in the referenced paper. These defects were assigned to gallium and oxygen vacancies. Characteristically, that gallium and oxygen vacancies are closely located each other, forming the associates [10].

The isolated oxygen vacancies can be restructured into F^+ or F-centers after trapping of one or two electrons. Oxygen vacancies $V_O^{\bullet\bullet}$ and associates of $(V_{Ga}V_O)'$ in β-Ga_2O_3 single crystals at high concentrations can create more complex aggregates kind of $(V_{Ga}V_O)'$-F^+ or $(V_{Ga}V_O)'$-F pairs. These aggregates can be responsible for blue or green emission in β-Ga_2O_3 [11].

Annealing of undoped β-Ga_2O_3 crystals in the oxygen atmosphere leads primarily to the healing of isolated oxygen vacancies. Apart of that, decreasing the concentration of interstitial gallium ($Ga_i^{\bullet\bullet\bullet}$) can be observed at crystals annealing due to Ga diffusion to gallium vacancies in associates or to the surface where after bonding with oxygen from the atmosphere the completion of the crystal occurs. Thus, a decrease in the number of oxygen vacancies and interstitial gallium and a less drastically decrease in the concentration of vacancies associates are expected after annealing in the oxygen atmosphere. A small increase of the transmission in the UV region is an evidence of that suggestion.

Incorporation of Mg^{2+} impurities in β-Ga_2O_3 crystals require charge compensation and are accompanied by the formation of additional oxygen vacancies. The blue coloration of the obtained β-Ga_2O_3 single crystals, as well as location of the long-wavelength edge of transparency, is caused by existing of a large number of small donors, free electrons, and deeper F-centers. In the equilibrium state, all deep and shallow traps are filled by charges.

The absorption band at 1.2 eV and photoconductivity in the near-IR region (600–1000 nm) is related with electronic transitions from filled F-centers to conduction band. The transitions of electrons from deep donors and trapped on shallow levels electrons to conduction band as well as absorption of free electrons can be responsible for absorption in the energy levels below 1 eV.

Shallow donors and part of the F centers are ionized in β-Ga_2O_3 crystals annealed in an oxygen atmosphere as well as in β-Ga_2O_3: Mg^{2+} crystals. The decrease of the concentration of shallow donors and isolated oxygen vacancies after annealing of β-Ga_2O_3 crystals in oxygen atmosphere leads to suppression of absorption in the IR-region at about 1.2 and 0.5–0.6 eV and shift of the long-wavelength edge of the transparency to 0.38 eV. Similarly, the ionization of shallow donors and some of the F-centers is a reason of transparency increase of β-Ga_2O_3: Mg^{2+} activated crystals in the 0.4–0.8 eV spectral region.

The interpretation of broad absorption and photoconductivity bands in UV spectral region is more complicated. The broad absorption and photoconductivity bands in 3.0–4.6 eV range that were found in as-grown β-Ga_2O_3 crystals, as well as excitation spectra of blue-green emission, can be assigned to electronic transitions from acceptor levels created by vacancy associates to the conduction band [12]. The existence of a set of acceptor levels with different depths can be assumed due to the presence of several positions of gallium and oxygen. As

a result, it should lead to a broad fuzzy absorption and photoconductivity bands.

The band of 3.8 eV, which appears at the magnesium doping of β-Ga_2O_3 crystals and increases with its concentration increase, apparently is caused by electron transitions from deep acceptor Mg^{2+} levels to the conduction band. A slight transparency increasing of β-Ga_2O_3 crystals in the UV spectral region 3.6–4.6 eV after annealing in an oxygen atmosphere can be due to a decrease in the concentration of $(V_{Ga}V_O)'$ vacancies associates of various types.

5. Conclusions

The absorption coefficient for as-grown β-Ga_2O_3 crystals, crystals annealed in an oxygen atmosphere as well as crystals activated with Mg^{2+} impurity crystals is growing rapidly in the UV spectral region and consistent with the formula for directly allowed transitions. The values of band gap energies are equal to $E_g = 4.98$ eV for $\boldsymbol{E}\|\boldsymbol{b}$ and 4.72 eV for $\boldsymbol{E}\perp\boldsymbol{b}$ orientations at 290 K and increase under the temperature lowering.

The negligible photoconductivity signal was detected in the background of dark current for as-grown β-Ga_2O_3 crystals. Thermal treatment of undoped crystals in the oxygen atmosphere or doping with Mg^{2+} ions leads to an increase of the resistivity of crystals in several times that decreases dark current and gives the opportunity to register the high signals of photoconductivity.

The position of photoconductivity bands is in good correlation with the absorption spectra in all spectral regions, as well as with position of the fundamental absorption edge. The bands in the UV and near-IR spectral region before fundamental absorption edge correspond to host defects of the crystal lattice and introduced impurity. Doping of β-Ga_2O_3 crystals with Mg^{2+} impurity leads to the appearance of additional broad UV absorption band with a maximum near 3.8 eV and IR absorption maximum in the vicinity of 1.2 eV. Electronic transitions from acceptors formed by gallium and oxygen vacancies into the conduction band are displayed as broad bands in the UV spectral region of 4.2–4.6 eV before the fundamental absorption edge were observed in optical absorption and photoconductivity spectra.

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