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Microdefects and Electrical Properties of β-Ga_2O_3 and β-Ga_2O_3:Mg Crystals Grown by Floating Zone Technique

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Microdefects in β-Ga_2O_3 and β-Ga_2O_3:0.1 % Mg single crystals grown by the method of floating zone technique with radiation heating have been studied. Porous defects with a tube-like shape were found on the (100) surface and in the bulk of undoped β-Ga_2O_3 crystals. Such defects are up to 1 μm in diameter and up to 100 μm in length, elongated along the [010] axis. Doping of gallium oxide with magnesium ions leads to a decrease in the concentration of defects and changes in their shape. The concentration and mobility of electrical charge carriers in undoped β-Ga_2O_3 crystals were calculated. The activation energies of the conductivity of the studied crystals were estimated. Some correlations between crystal growing conditions, doping, and the rate of Ga_2O evaporation from the melt and defect density were revealed and discussed, providing aspects for further material development. The mechanisms of these defects formation have been also analyzed.

Keywords: β-Ga_2O_3 and β-Ga_2O_3:Mg single crystals, Microdefects, Conductivity, Charge carrier concentration, Activation energy.

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1. INTRODUCTION

Gallium oxide β-Ga_2O_3 belongs to the semiconductor oxide family and is an attractive material with a wide bandgap, $E_g \sim 4.8$ eV. The applicability of β-Ga_2O_3 single crystals is promising in different areas, including Schottky diodes (SBDs), metal-semiconductor (MESFETs) and metal-oxide-semiconductor (MOSFETs) transistors [1, 2], transparent electrodes [3], gas sensors [4, 5] and solar blind photodetectors for optoelectronic devices operating in the far ultraviolet spectral region [6, 7]. In addition, due to the attractive luminescence properties, β-Ga_2O_3 has attracted considerable attention for its application in phosphors, displays, and scintilators [8-10].

In recent years, the technology for β-Ga_2O_3 crystals growing has been significantly improved, and high-quality single crystals up to 2-4 inches in diameter have been grown by the Czochralski [11] and EDF [12] methods. However, crystals of wide bandgap semiconductors often contain point defects, microdefects, micropipes that penetrate into the crystals. Such defects and their complexes can create traps and recombination centers that affect the operation of devices [13, 14]. It can cause a decrease in the breakdown voltage and excessive dark current of transistors, a reduced sensitivity of photodetectors, and a decrease in the efficiency of devices.

Therefore, defect control is an important problem in the development of β-Ga_2O_3 crystal-grown technology, since defects negatively affect the performance of crystal-based devices. To establish the nature of the appearance of defects in gallium oxide, it is necessary to study the effect of impurities and growing conditions on the properties of crystals. For such tasks, it is good to use the floating zone technique, because it allows you to grow small crystals at a low cost of resources.

The aim of this work is to grow β-Ga_2O_3 crystals by the floating zone technique with radiation heating and to study microscopic defects that occur in crystals.

2. EXPERIMENTAL DETAILS AND RESULTS

2.1 Sample Preparation and Characterization

The floating zone technique with radiation heating is an attractive method for growing small crystals due to its low cost and high manufacturability. The 4N purity Ga_2O_3 raw materials for crystals growing were preheated in a muffle furnace at a temperature of 1000 °C for several hours to remove water. Mass losses of raw materials due to such heat treatment were in the range of 0.5-2 %. A magnesium impurity was also added to the charge in the form of MgO, the mole fraction of which was 0.1 mol. %. Mixtures of oxides were mechanically ground in an agate mortar for 21 h. For better homogenization of the powder mixture, ethyl alcohol was used in an amount sufficient to form a paste. Rods with a diameter of 6-8 mm and a length of 90 mm were pressed from the mixture of oxides with the addition of 1-2 % polyvinyl ethyl alcohol as a plasticizer. Steel molds were used to press the rods. The pressed polycrystalline rods were placed in an electric furnace on platinum foil. The rate of temperature rise in the furnace was 165 °C/h. The rods were sintered in air for 50 h at a temperature of 1300 °C. The temperature in the furnace was maintained by a RT-0102.

Gallium oxide single crystals were grown from sintered rods. Crystals were grown in ambient air in the direction of the [010] axis. The growth speed was 2-8 mm/h and the rotation speed was 6 rpm. Unintentionally doped (UID) and magnesium-doped β-Ga_2O_3 crystals were grown. It should be noted, that

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during the growing of undoped β-Ga_2O_3 crystals, intense evaporation from the melt zone was observed. The evaporation product was dark gray and settled on the elements of the growth chamber. XRD studies showed that the product of evaporation was gallium oxide Ga_2O. At the same time, such intense evaporation of Ga_2O was not observed during the growth of magnesium-doped β-Ga_2O_3 crystals.

Fig. 1 shows photos of as-grown and Mg^{2+}-doped β-Ga_2O_3 crystals. The length of the grown β-Ga_2O_3 crystals was 20-30 mm and the diameter was 6-8 mm. β-Ga_2O_3 crystals have two ideal cleavage planes, (100) and (001), and the crystals cleaved relatively easily along these planes. This made it possible to obtain for study very thin (up to 15-20 microns) plane-parallel single-crystal gallium oxide plates and greatly simplified the orientation of the crystals. When the direction of crystal growth coincided with the crystallographic axis *b* of the crystal, the (100) plane was usually the twinning plane. As a rule, the twinning plane was not observed in β-Ga_2O_3 crystals grown in the direction perpendicular to the (100) plane.

The undoped β-Ga_2O_3 crystals were blue, the intensity of which varied from a weakly blue at the beginning of the crystal to a darker one at the end of the grown crystal (Fig. 1a). The blue color of the crystals is due to the intense optical absorption bands in the red and near-infrared spectral regions [15, 16]. Optical absorption is due to the transitions of electrons from the levels of oxygen vacancies and shallow donors to the conduction band [15, 16], as well as the absorption of free electrons [11]. β-Ga_2O_3:Mg crystals were colorless (Fig. 1b).

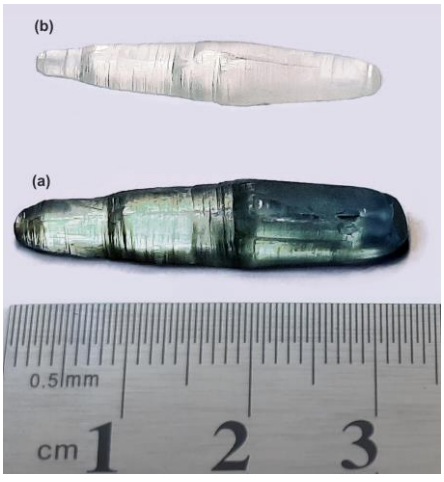

Fig. 1 – Images of as-grown UID β-Ga_2O_3 (a) and β-Ga_2O_3: 0.1 % Mg (b) crystals grown by floating zone technique

2.2 Studies of Microdefects

The method of selective chemical etching was used to detect microdefects on the crystal surface and to evaluate the structural perfection of β-Ga_2O_3 and β-Ga_2O_3:0.1 % Mg crystals. The best results were obtained for chemical etchant consisting of equal parts of concentrated acids $H_3PO_4 + H_2SO_4$. Etching was performed by immersing the crystal in the solution for 2 min. The optimal etching temperature was ~ 175 °C. β-Ga_2O_3 crystal samples were washed in distilled water and dried on filter paper after etching.

We used optical microscopy to investigate surface defects and their density distribution. Etched or cleaved β-Ga_2O_3 single-crystal plates were investigated on a LUMAM I-3 microscope.

Fig. 2 shows typical surface (100) images of undoped β-Ga_2O_3 (a) and β-Ga_2O_3:0.1 % Mg^{2+} (b) single crystals. A number of line-shaped defects were detected on the (100) plane of undoped as-grown gallium oxide samples. As can be seen from the presented images, the detected microscopic defects have a linear character with a length from 5 to 100 μm. The width of these linear defects was about 1-2 μm. Defects extend mainly in the direction of the [010] crystal axis. It should be noted that linear defects were observed not only on the etched surface of the crystal. Similar defects of a linear shape were also visible in the inner regions of the single crystal plate. Such linear defects were the main microdefects in undoped β-Ga_2O_3 crystals. They are cavities in the volume of the β-Ga_2O_3 crystal. The density of microdefects measured in several areas on the front of the undoped β-Ga_2O_3 crystal plate surface was equal to $5 \cdot 10^4$ cm^{-2}.

The image of the surface of the Mg-doped β-Ga_2O_3: 0.1 % Mg^{2+} crystals is presented in Fig. 2b. In contrast to undoped crystals, in as-grown β-Ga_2O_3:0.1 % Mg^{2+} crystals, there are mainly point microdefects, which have the form of quadrangular pyramids. The density of microdefects on the β-Ga_2O_3:0.1 % Mg^{2+} crystal plate surface was 2.3×10^3 cm^{-2} and is much lower than the density of microdefects in undoped β-Ga_2O_3 crystals.

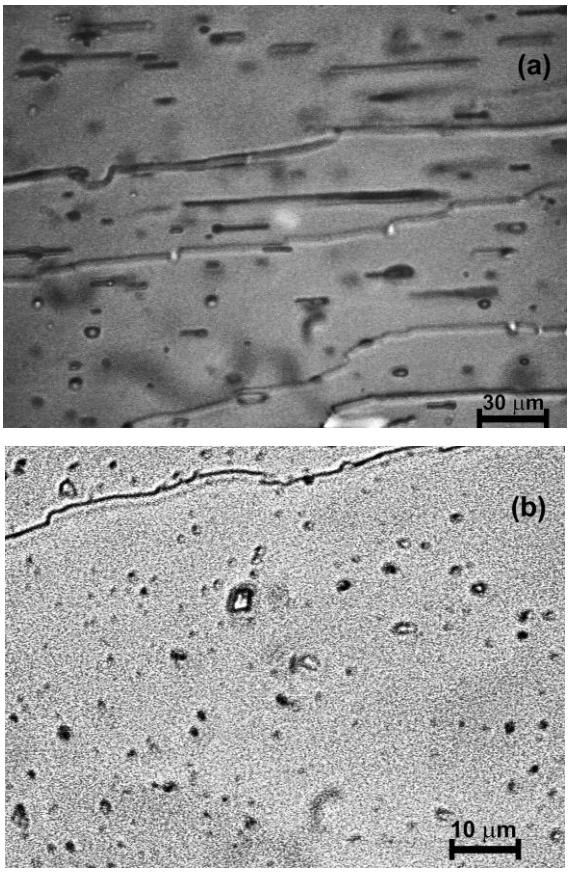

Fig. 2 – Surface images of the (100) plane of the as-grown UID (a) and Mg dopped (b) β-Ga_2O_3 single crystals

2.3 Electrical Properties

Conductivity studies were performed to determine the concentration of free electrons and to evaluate the quality of the as-grown β-Ga_2O_3 crystals. Samples of gallium oxide single crystals for electrical conductivity studies were obtained by cleaving the single crystal along the (100) plane. Electrical contacts for conductivity measuring were obtained by radio frequency (RF) sputtering of titanium. Four-probe van der Pauw method was used to measure the conductivity of low resistivity undoped β-Ga_2O_3 samples. The electrical conductivity of high-resistance β-Ga_2O_3:0.1 % Mg samples was measured by two probe method with an electrometer B7-30.

Hall voltage measurements were performed to calculate the electron concentration in undoped β-Ga_2O_3 crystals at two fixed temperatures of 110 and 293 K. The dependence of the Hall voltage on the magnetic field strength was also studied. Within the changes from 0 to 0.70 T of the magnetic field strength, this dependence turned out to be linear. The Hall constant R was calculated from the average voltage at a fixed value of the magnetic field. The electrical carrier concentration calculated by the formula $n = 1/(R - e)$ was $1.25 \cdot 10^{18}$ and $1.80 \cdot 10^{18}$ cm^{-3} at 110 and 293 K, respectively. The electrical conductivity of the as-grown UID β-Ga_2O_3 crystals was quite high and reached 2.5 $Ohm^{-1} \cdot cm^{-1}$ at 293 K. It did not change much in the temperature range from 110 to 200 K, and at higher temperatures, there was a weak temperature dependence of the conductivity. The activation energy of the electrical conductivity, calculated from the linear dependence $\ln I = f(1000/T)$ in the temperature range 273-360 K, was about ~ 0.025 eV (Fig. 3, blue squares). The activation energies of the conductivity for Mg-doped high-resistance β-Ga_2O_3:0.1 % Mg crystals were at about ~ 0.84 eV (Fig. 3, red squares). The mobility of charge carriers was calculated using the values of charge carrier concentration (n) and electrical conductivity (σ). At temperatures of 110 and 293 K, the mobility of charge carriers was 180 and 140 $cm^2 \cdot V^{-1} \cdot s^{-1}$, respectively. The negative sign of the Hall constant indicates n-type conductivity. In contrast to undoped β-Ga_2O_3 crystals, magnesium-doped β-Ga_2O_3:0.1 % Mg crystals were high-resistivity. Their resistivity exceeded 10^8 ohm·cm.

3. DISCUSSION

Microdefects similar to the linear defects described above were previously observed in β-Ga_2O_3 crystals grown by the Bridgman and EFG methods [15, 17]. Nakai et al. [15] called such microdefects "nanotubes" and admitted that they are essentially cavities in the crystal volume. It also follows from our research that inside these linear defects, there are cavities that arise in the crystal during the growth.

We detected a big difference in the behavior of the gallium oxide melt zone when undoped or magnesium-doped crystals are grown. As noted above, the growth of β-Ga_2O_3:Mg crystals is accompanied by insignificant evaporation of Ga_2O from the melt, while strong evaporation is observed during the growth of undoped β-Ga_2O_3 crystals. The density of microdefects on the surface of the β-Ga_2O_3:0.1 % Mg^{2+} crystal plate was approximately 10 times less than the density of microdefects in undoped crystals. Therefore comparing the concentration of linear defects in undoped β-Ga_2O_3 crystals grown under strong evaporation and β-Ga_2O_3:Mg crystals obtained with weak evaporation, it can be seen that there is a correlation between the concentration of linear microdefects and the rate of evaporation of raw materials during crystal growth.

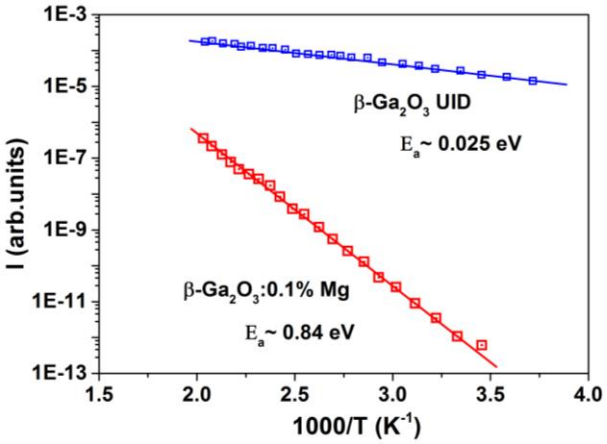

Fig. 3 – Temperature dependences of the conductivity of undoped β-Ga_2O_3 (blue squares) and β-Ga_2O_3:0.1 % Mg (red squares) crystals

Partial dissociation of β-Ga_2O_3 into volatile Ga_2O oxide and oxygen O_2 ($Ga_2O_3 \rightarrow Ga_2O + O_2$) when it is heated to temperatures above 1000 °C in an atmosphere with a low partial pressure of oxygen is a characteristic feature of gallium oxide. The growth of gallium oxide crystals usually occurs in conditions with a lack of oxygen. Under these conditions, a large concentration of point defects is formed. When oxygen leaves the crystal, an oxygen vacancy is formed. It can be assumed that the loss of oxygen is essentially the first step in the formation of the Ga_2O nanoclusters in β-Ga_2O_3 crystals. Subsequent sublimation of Ga_2O nanoclusters leads to the formation of a nanocavity in the crystal in the form of three oxygen V_O and two gallium V_{Ga} vacancies. Note that this formation of two gallium vacancies and three oxygen vacancies is electrically neutral and energetically advantageous. Such nanocavity formation can be considered as the nucleus of a growing negative crystal (or cavity) formed in the volume of the crystal. Oxygen and gallium atoms, which are located on the walls of the cavity, have lower binding energy, so they can leave the crystal in the first place. Thus, the formation of a microcavity inside the crystal contributes to the additional loss of oxygen and gallium atoms that are located on the walls of the cavity. This can lead to an avalanche-like formation of new gallium and oxygen vacancies on the walls of the nanocavity and contributes to an increase in its size. In other words, the microcavities increase in size during crystal growth. Since such a mechanism of microcavity formation involves the growth of linear microdefects due to the formation of new vacancies of gallium and

oxygen on the walls of the cavity, such microdefects should be oriented in directions where atoms with less energy of defect formation are located. Their form and linear size will be determined by the growth rate of the crystal. Strong anisotropy of the growth rate of β-Ga_2O_3 crystals leads to a characteristic geometric shape of the linear defect. The crystal grows in the [010] direction much faster than in other directions. In [15], it was also noted that the size of the linear defect in each direction is uniquely tied to the anisotropy of the growth rate. Therefore, the large size of the defect in the [010] direction is associated with a high growth rate in this direction. Similarly, the medium size of the defect is in the [001] direction and the short size is in the [100] direction.

The undoped β-Ga_2O_3 crystals were low resistivity. The high conductivity of crystals is due to shallow donors created by uncontrolled impurities of Si, Sn, Ge [2, 18] or interstitial gallium [13, 14]. Interstitial gallium is formed due to the loss of oxygen during crystal growth. As the β-Ga_2O_3 crystal grows, Ga_2O diffuses from the volume to the crystal surface and sublimates. This movement of gallium atoms contributes to the formation of numerous defects in gallium oxide, in the form of interstitial gallium Ga_i. Consequently, after cooling the grown crystal to room temperature, it has a high concentration of point defects in the form of interstitial gallium and, therefore, high electrical conductivity. Point defects in the form of interstitial gallium are natural donors in gallium oxide [13, 14] and together with donors of tetravalent silicon [2, 18] are responsible for the high conductivity of undoped β-Ga_2O_3 crystals.

Mg-doped β-Ga_2O_3 crystals were high-resistivity. Doping of gallium oxide with Mg^{2+} impurity, on the one hand, leads to the formation of additional oxygen vacancies [19], and on the other hand, creates acceptor levels near the top of the valence band, which compensate for shallow donor levels. In addition, there is low evaporation of Ga_2O during β-Ga_2O_3:Mg^{2+} crystal growth, and therefore significantly fewer defects in the form of interstitial gallium are formed. Thus, the conductivity of high-resistance β-Ga_2O_3:Mg^{2+} crystals is controlled by the release of electrons from deep levels created by oxygen vacancies [19] or iron ions [20] and is therefore low.

4. CONCLUSIONS

Single crystals of β-Ga_2O_3 have been grown by the floating zone technique. During the growth of undoped β-Ga_2O_3 crystals in ambient air, intense evaporation of Ga_2O from the melt zone was observed. As a result, such undoped crystals have a high density of linear microdefects as well as high electrical conductivity. When growing crystals doped with a magnesium impurity, only weak evaporation of Ga_2O from the melt was observed, and grown crystals had a lower density of linear microdefects and a high resistance. Undoped β-Ga_2O_3 crystals are an n-type semiconductor with a charge carrier concentration of up to $1.8 \cdot 10^{18}$ cm^{-3} and a mobility of 140 $cm^2 \cdot V^{-1} \cdot s^{-1}$ at room temperature. Doping with 0.1 % Mg leads to a sharp increase in the resistance of β-Ga_2O_3:0.1 % Mg crystals. The activation energies of the conductivity for undoped low-resistance β-Ga_2O_3 crystals and Mg-doped high-resistance β-Ga_2O_3:0.1 % Mg crystals are at about 0.025 and 0.84 eV, respectively.

The mechanism of formation of line-shaped microdefects due to oxygen loss and subsequent avalanche formation of nanoregions of Ga_2O and their subsequent sublimation is proposed. The high conductivity of as-grown crystals is also a consequence of oxygen loss and the formation of point defects in the form of interstitial gallium ions. Doping of gallium oxide with an impurity of Mg^{2+} leads to the formation of additional oxygen vacancies and creates acceptor levels near the top of the valence band, which compensate for shallow donor levels, reducing herewith the electrical conductivity.

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Мікродефекти та електричні властивості кристалів β-Ga_2O_3 та β-Ga_2O_3:Mg, вирощених методом зонної плавки

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Досліджено мікродефекти в монокристалах β-Ga_2O_3 і β-Ga_2O_3:0.1 % Mg, вирощених методом оптичної зонної плавки з радіаційним нагріванням. На поверхні (100) та в об'ємі нелегованих кристалів β-Ga_2O_3 виявлено пористі дефекти трубоподібної форми. Такі дефекти мають діаметр до 1 мкм і довжину до 100 мкм, витягнуті по осі [010]. Легування оксиду галію іонами магнію приводить до зменшення концентрації дефектів та зміни їхньої форми. Розраховано концентрацію та рухливість носіїв електричного заряду в нелегованих у β-Ga_2O_3 кристалах. Оцінено енергії активації провідності досліджуваних кристалів. Виявлено та обговорено певні кореляції між умовами вирощування кристалів, легуванням і швидкістю випаровування Ga_2O з розплаву та густиною дефектів, що надає аспекти подальшого розвитку матеріалу. Також проаналізовано механізми утворення цих дефектів.

Ключові слова: Монокристали β-Ga_2O_3 та β-Ga_2O_3:Mg, Мікродефекти, Провідність, Концентрація носіїв заряду, Енергія активації.