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Electric properties of Cr_2O_3:Mg grown by epitaxy on the sapphire and gallium oxide substrates

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Electrical properties of Cr_2O_3 layers with improved *p*-type conductivity by doping them with magnesium (0.1 wt.% to 5 wt.%) in the process of mist CVD epitaxy on sapphire substrates and single crystals of bulk gallium oxide (β-Ga_2O_3) with *n*-type conductivity are studied. In the capacitance-voltage characteristics of heterojunctions, the concentration of Nd donors ($1.2 \cdot 10^{17}\,cm^{-3}$) is observed. In the admittance spectra, clearly distinguishable peaks are observed corresponding to states with energies of 0.15 eV, 0.19 eV, 0.32 eV, 0.62 eV. They are associated with the recombination of electrons from β-Ga_2O_3 with holes in the *p*-layer, with the need to overcome a large band gap in the conduction band of the heterointerface, and with the formation of interface states in the β-Ga_2O_3 layer.

Keywords: $p-n$-heterojunction, gallium oxide, chromium oxide, electrophysics.

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1. Introduction

Thermostable gallium oxide polymorph β-Ga_2O_3 is a promising ultra-wide-band semiconductor (~ 4.8 eV) for mass production of power diodes and solar-blind photodetectors of a new generation [1–3]. Its main advantage relative to other ultra-wide-band materials (diamond, AlN, BN) is the possibility of obtaining large, chemically pure or alloyed single crystals of high quality by growth methods from its own melt (Czochralski, Stepanov, vertical Bridgman), i. e. suitable for the production of substrates for epitaxy [4].

However, the „smooth“ top of the valence band characteristic of transparent semiconductor oxides [5] makes it difficult at the moment to obtain *p*-type conductivity in Ga_2O_3 to create homoepitaxial $p-n$-junctions and bipolar transistors. Nevertheless, recent studies [6] of power diodes based on gallium oxide heterostructures with other wide-band materials of *p*-type have demonstrated a significant improvement in operating parameters and achieved record values not only for gallium oxide, but also for semiconductors in principle, breakdown voltage of 13.5 kV for NiO/β-Ga_2O_3 heterostructures [7]. Nevertheless, the increased density of defects at the interface and the relatively low radiation resistance of NiO/β-Ga_2O_3 actualizes the study of other variants of heterojunctions [8–10].

Over the past two decades, against the background of success in epitaxy and doping experiments, interest has grown in chromium oxide (III) Cr_2O_3as a wide-band ($3-3.3$ eV) a semiconductor material with a natural *p*-type of conductivity. A significant increase in electrical conductivity in thin layers of Cr_2O_3 was demonstrated in Ref. [11] with the introduction of impurity atoms Mg, Ni and Cu up to 10^1 S/m. The impurities were characterized by the appearance of a fine acceptor state with an energy of ~ 0.2 eV. It is assumed that it has a polaronic nature, since the properties of the level do not depend on the type of impurity atom. A power $p-n$-diode was obtained in recent study in Ref. [12] by pulse laser deposition (PLD) of Cr_2O_3:Mg on the commercial template Novel Crystal Technologies (001) HVPE β-Ga_2O_3/EFG β-Ga_2O_3:Sn. It was shown to be able to function at a temperature of up to 600 °C and a breakdown voltage of ~ 390 V.

On the other hand, Cr_2O_3 has a corundum structure, which makes it isomorphic to commercial sapphire substrates and the main metastable polymorph of gallium oxide, α-Ga_2O_3, with which it also forms a continuous series of solid solutions [13,14]. $p-n$-heterostructures with a high concentration of acceptors for a certain concentration range Iridium can be obtained for a similar case of solid solutions α-$(Ir_xGa_{1-x})_2O_3$ as shown in Ref. [15]. Ga_2O_3 heterostructures with Cr_2O_3 are more promising for commercial implementation considering the cost and complexity of buying iridium, as well as the large band gap of Cr_2O_3 [14].

Thus, two directions can be distinguished in the creation of $p-n$-heterojunctions of *n*-Ga_2O_3 with *p*-Cr_2O_3: obtaining doped layers of Cr_2O_3 on commercial sapphire substrates to be used as templates for the epitaxy of alloyed α-Ga_2O_3 and the production of $p-n$-heterostructures of *p*-Cr_2O_3

with β-Ga_2O_3 substrates obtained by melt growth methods. The electrical characteristics of two types of samples are considered in this paper: Cr_2O_3:Mg on c-sapphire and $p-n$-heterojunctions of Cr_2O_3:Mg/(100) β-Ga_2O_3.

2. Experimental procedure

Cr_2O_3:Mg layers were grown by ultrasonic chemical vapor deposition (mist-CVD) [2] under the same conditions, at a temperature of $\sim 500\,^\circ$C. The growing was conducted in a reactor with hot walls. Chromium acetylacetonate pairs Cr(acac)$_3$ [14], magnesium Mg(acac)$_2$ of our own production and oxygen gas were used as precursors. Argon served as a carrier gas for the vapors. The growth rate was $\sim 1\,\mu$m/h. The resulting films had a thickness of $\sim 1\,\mu$m. The set concentration of magnesium in the films varied from 0.1 to 5 wt.% in the original precursor mixture. Epitaxy was performed on sapphire substrates (0001) and plates of unalloyed crystals β-Ga_2O_3, gouged along a plane of very perfect cleavage (100). Bulk crystals of β-Ga_2O_3 were grown by the Czochralski method, and their electrical properties were studied earlier in Refs. [16,17].

Round contacts with a diameter of 1 mm were applied for measurements on the surface of films Cr_2O_3:Mg/c-sapphire: Ni-Schottky diodes (30 nm) and ohmic Ti/Au (20/80 nm). A solid ohmic contact Ti/Au (20/80 nm) was additionally applied to the crystal from the reverse side in the case of Cr_2O_3:Mg/β-Ga_2O_3-heterojunctions. Electrical characteristics were measured in the dark and illuminated by LEDs with a wavelength in the range of 277–940 nm at a temperature of 80–400 K. The dependences of capacitance on frequency, AC capacitance and conductivity on frequency and temperature (admittance spectra), as well as deep-level relaxation spectroscopy (DLRS) spectra were studied. The methods are described in detail in Refs. [8,18,19].

3. Results and discussion

The measurement of volt-ampere characteristics (VAC) at different temperatures both between ohmic contacts and between Schottky diodes or between Schottky diodes and ohmic contacts for Cr_2O_3 films on sapphire invariably gave linear dependences of current on voltage with a weak dependence of current on illumination by a set of LEDs with wavelengths from 277 to 940 nm (Figure 1, *a*). The temperature dependence of the current is shown in Figure 1, *b* and is characterized by an activation energy of 0.225 eV.

A good rectification was observed in Cr_2O_3:Mg/β-Ga_2O_3 structures in volt-ampere characteristics measured between the ohmic contact to the Cr_2O_3 film and the substrate (100) β-Ga_2O_3 with low reverse current that increased with increasing Mg concentration in Cr_2O_3, low series resistance in the direct branch, R_s, decreasing with increasing magnesium concentration, and the ideality factor in the direct branch $\eta = 2$ (Figure 2, *a*). Dependencies of $1/C^2$ (C — structure

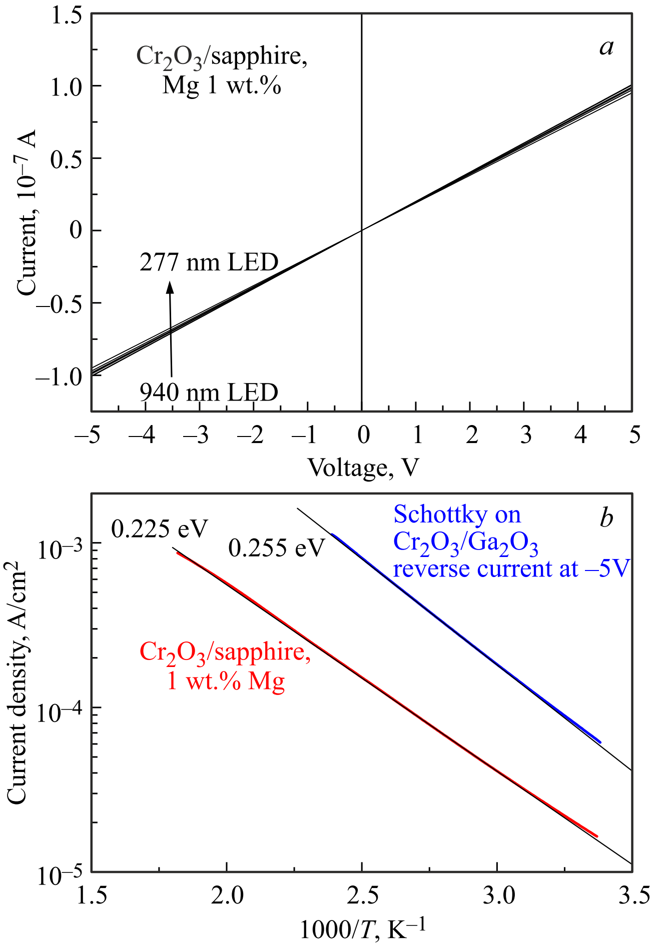

Figure 1. *a* — VAC of Cr_2O_3:Mg layer (Mg = 1 wt.%) on sapphire, measured at room temperature in the dark and with illumination by LEDs with different wavelengths (VAC in the dark and in case of illumination by an LED with a wavelength of 940 nm coincide); *b* — temperature dependence of the current at 5 V the layer on sapphire and the reverse current for the sample on the bulk crystal of β-Ga_2O_3.

capacity) on the applied voltage B were linear (Figure 2, *b*). The voltage cutoff value was 2.6 V, the concentration of donors, N_d, calculated from the slope of the straight line in Figure 2, *b*, was $1.2 \cdot 10^{17}\,\text{cm}^{-3}$. This is a typical voltage-capacitance dependence for an unbalanced heterojunction of p-Cr_2O_3(Mg)/n-Ga_2O_3, in which the width of the space charge region (SCR) is determined by a more weakly doped region n-Ga_2O_3 (the concentration measured from the slope is close to the typical concentration of residual donors in our bulk crystals Ga_2O_3 [16,17]), and the voltage cutoff value corresponds to a gap in the valence band between p^+-Cr_2O_3 and n-Ga_2O_3 [12].

Clearly distinguishable peaks are observed in the dependences dC/dT (in the admittance spectra) corresponding to states with energy 0.15, 0.19, 0.32, 0.62 eV (Figure 2, *c*). DLRS spectra (Figure 2, *d*) show peaks associated with the centers $E2$ ($E_c - 0.8$ eV), $E3$ ($E_c - 1.1$ eV)

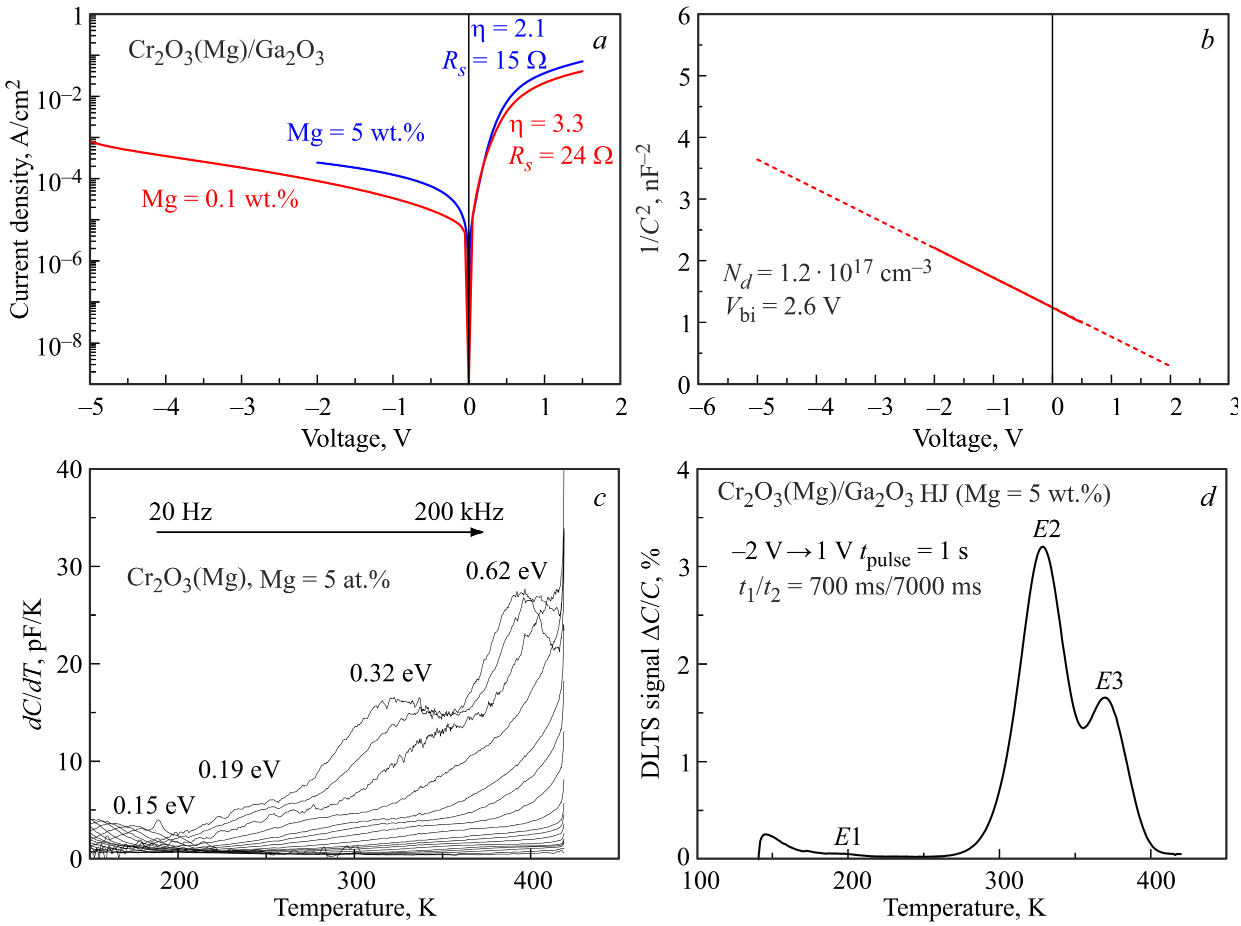

Figure 2. *a* — VAC measured at room temperature of *p*–*n*-heterojunctions of Cr_2O_3:Mg/β-Ga_2O_3 with two different magnesium concentrations; *b* — dependence of $1/C^2$ on the voltage for the Cr_2O_3:Mg/β-Ga_2O_3 heterojunction with a magnesium concentration of 5 wt.%, measured at room temperature; *c* — temperature dependence of the temperature derivative of the capacitance for frequencies in the range of 20 Hz–200 kHz for a sample with a magnesium concentration of 5 wt.%; *d* — heterojunction spectrum with a magnesium concentration of 5 wt.%, measured at a frequency of 10 kHz, at a voltage of −2 V, an enriching pulse of 1 V with a duration of 1 s; the spectrum is shown for time windows of 700/7000 ms.

and $E1$ ($E_c - 0.6$ eV), characteristic of our single crystals β-Ga_2O_3 and attributed in the literature to iron acceptors, gallium substitutes, oxygen vacancies and complexes of silicon with hydrogen [20].

4. Conclusion

Thus, magnesium-doped layers of Cr_2O_3 were grown for the first time by the mist-CVD (Mist Chemical Vapor Deposition) method on a sapphire substrate and plates of (100) β-Ga_2O_3 obtained by growing from the melt. Although it was not possible to obtain a diode structure with metal contacts for Cr_2O_3:Mg on sapphire, an increase in electrical conductivity will allow using them as templates for growing α-Ga_2O_3:Sn of *n*-type. Good rectification in Cr_2O_3:Mg/β-Ga_2O_3 made it possible to study the spectra of deep centers using admittance spectroscopy and deep level relaxation spectroscopy for the first time for this heterojunction. The results obtained demonstrate the proximity of the electronic properties of Cr_2O_3:Mg/β-Ga_2O_3 to the previously studied *p*–*n*-diode NiO/β-Ga_2O_3 [17]. The low leakage current and the ideality factor close to 2 were associated in the latter with the need to overcome a large band discontinuity in the conduction band of the heterointerface and with the recombination of electrons from β-Ga_2O_3 with holes in the NiO layer, as well as with the formation of interface states in the β-Ga_2O_3 layer [9,17].

It is worth noting separately that the possibility of obtaining a conductive Cr_2O_3:Mg layer by the mist-CVD method on the surface of the plate (100) β-Ga_2O_3 with the formation of a functional *p*–*n*-structure is promising because mist-CVD is a relatively inexpensive and fast epitaxy method, and the use of a very perfect cleavage surface (100) will significantly simplify the production of substrates from bulk crystals Ga_2O_3. At the same time, it was reported that *p*-Cr_2O_3(Mg)/*n*-Ga_2O_3 heterojunctions can remain operational at very high temperatures of $\sim 600\,°C$ [12]. We are currently conducting experiments aimed at determining the maximum temperatures up to which such heterojunctions can be used. But it will be especially interesting to grow $p-n$-heterojunctions of α-Cr_2O_3(Mg)/α-Ga_2O_3 where it is possible to take full advantage of the isomorphism of these two semiconductors with similar lattice parameters in order to avoid the formation of interface defects at the heterogeneous boundary, which can be formed in case of growth on a monoclinic β-Ga_2O_3 [8,17].

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Conflict of interest

The authors declare that they have no conflict of interest.

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