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The α-Cr_2O_3 layers grown on (100) β-Ga_2O_3 substrates by ultrasonic vapor chemical epitaxy (mist-CVD)

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Heterocontacts based on α-Cr_2O_3/β-Ga_2O_3 have recently attracted interest, as they enable realizing in device structures the potentials of such an ultra-wide-bandgap semiconductor as gallium oxide; the matter is that it is yet impossible to obtain gallium oxide samples of the p-type conductivity with the parameters suitable for instrumental applications, while this is quite achievable for α-Cr_2O_3. In this work, epitaxial chromium oxide layers on bulk gallium oxide substrates up to $1\,\mu$m and more thick were obtained by the CVD method for the first time. The question of orientation of these layers was considered. X-ray diffraction has revealed that the α-Cr_2O_3 layers grown on (100) β-Ga_2O_3 wafers exhibit a single layer reflex corresponding to $(11\bar{2}6)$.

Keywords: gallium oxide, chromium oxide, mist-CVD epitaxy, heterostructures, multilayer films.

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This study was stimulated by publications on heterocontacts based on α-Cr_2O_3/β-Ga_2O_3 [1,2]. Note that in [2] there was successfully realized a vertical diode structure combining a Cr_2O_3 layer doped with Mg which provided the p-type conductivity, and n-type β-Ga_2O_3 layer doped with Si which was obtained in the process of HVPE homoepitaxy on the (001) β-Ga_2O_3 wafer; this structure had high breakdown voltage $U_B = 390$ V and, in addition, withstood high-temperature tests, during which it retained functional properties without noticeable changes under repeated heating up to 600 °C. In both cited works, methods for applying the α-Cr_2O_3 layer were of the vacuum-deposition type: magnetron sputtering [1] and pulsed laser deposition (PLD) [2]. The film deposition rates in both cases were low, and, hence, thicknesses of the deposited layers were significantly less than $1\,\mu$m, which might be insufficient for a high-voltage diode with $U_B > 1000$ V. To our mind, ultrasonic chemical vapor deposition (mist-CVD epitaxy) is best suited for depositing chromium oxide films and creating α-Cr_2O_3/β-Ga_2O_3 heterocontacts. This method provides the highest-quality α-Cr_2O_3 layers on sapphire substrates [3–5].

Bulk single crystals for the β-Ga_2O_3 substrates were fabricated by the Czochralski method. Substrate wafers $\sim 0.5-1$ mm thick were chipped out from these crystals along cleavage planes (100). Earlier it has been shown that those wafers have electronic conductivity sufficient to form heterocontacts; this was demonstrated for the case of p-NiO/n-Ga_2O_3 [6].

In this study, the α-Cr_2O_3 layers were grown in an original-design reactor for mist-CVD epitaxy with a 2.4 MHz ultrasonic emitter capable of providing vapor droplets 10–100 nm in size [7]. Cr_2O_3 was synthesized by using aqueous solution of $Cr(acac)_3$ (0.04 mol/l) prepared by our own technique, whose vapor was fed from the emitter by transport gas (Ar) into a tightly sealed quartz reactor with hot walls. Oxygen was supplied through the second channel. The chromium oxide film was formed directly on the wafers of bulk β-Ga_2O_3 crystals having sufficiently large areas of atomically smooth surface (i.e., suitable for epitaxy). The growth experiments were performed at two deposition-zone temperatures: 500 and 800 °C. The process duration was 1–2 h. In some cases, the low-temperature layers were annealed at 800 °C.

Results of studying electrophysical properties of the obtained chromium oxide heterostructures on conductive

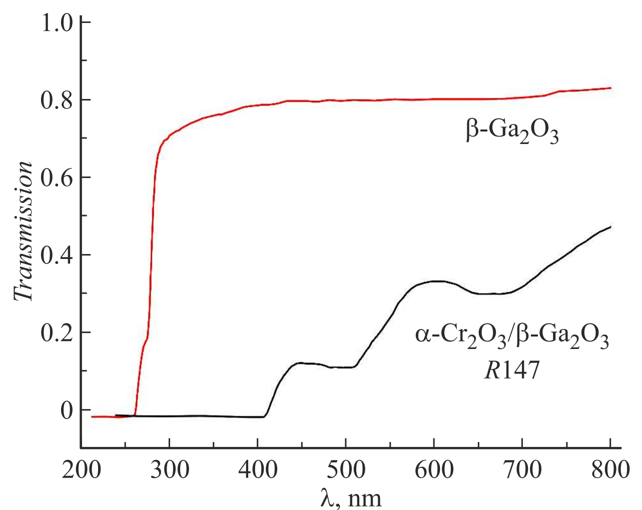

Figure 1. Optical transmission spectra of the (100) β-Ga_2O_3 wafer covered by the α-Cr_2O_3 layer grown at 500 °C.

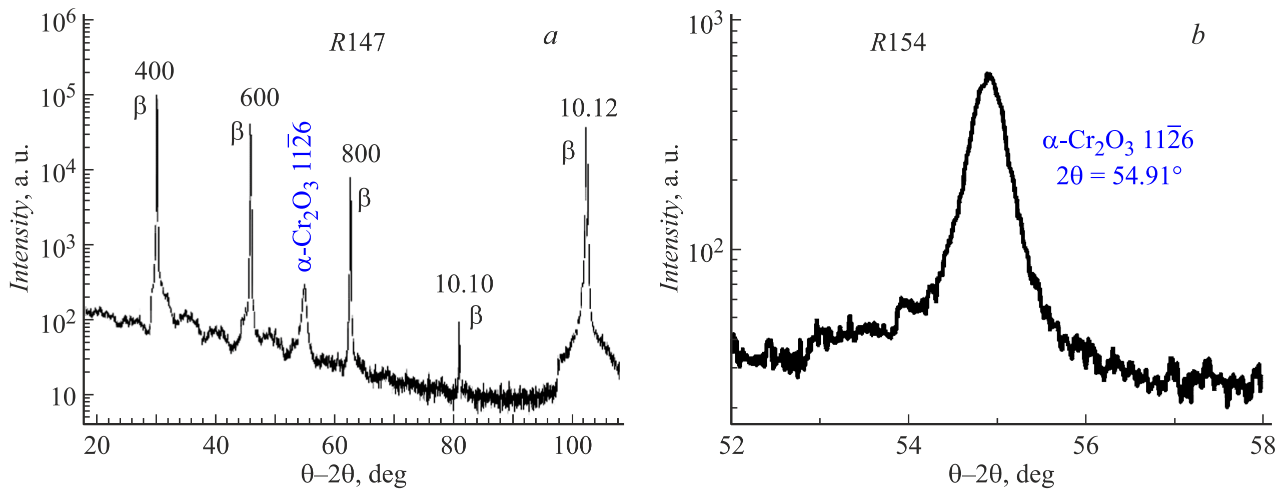

Figure 2. Diffraction patterns of two α-Cr_2O_3/β-a_2O_3 samples: *a* — *R*147 grown at 500 °C, *b* — *R*154 grown at 800 °C.

X-ray diffraction data for Cr_2O_3/β-Ga_2O_3

Sample	Process parameters	FWHM,°	*hkil*
*R*149	$T_g = 800\,°C$	1.5	$11\bar{2}6$
*R*156	$T_g = 500\,°C$, annealing at 800 °C	4	$11\bar{2}6$
*R*204	$T_g = 500\,°C$ $Cr_2O_3 : 0.5\%$ Mg	more than 10	$11\bar{2}6$

gallium oxide substrates will be presented in the next publication.

Initially undoped chromium oxide layers have very low electrical conductivity ($\sim 10^{-3}$ S/m) [8]. In the experiments performed, it was increased due to doping in the process of epitaxy with Mg, Ni or Cu by adding relevant acetylacetonates to the initial solution. To evaluate the electrical resistance in epitaxial processes, jointly with β-Ga_2O_3 there were used basic-orientation sapphire wafers on which Cr_2O_3 was also grown concurrently. This was done in order to eliminate the influence of high electrical conductivity of the β-Ga_2O_3 substrates [6]. Preliminary electrical resistance measurements with megohmmeter MEGEON 13225 (GRSI RF 74507-19) at room temperature and mechanically fixed 4-mm distance between the samples have demonstrated its decrease from $10^6 - 10^8$ to $10^2 - 10^3\,\Omega$ (results for Cu and Ni are available in the conference proceedings [9]). On the other hand, a more comprehensive study of electrical conductivity has not yet been accomplished because of the need to properly select ohmic and Schottky contacts; therefore, in this work we restrict ourselves to obtaining results of structural studies and clarifying specific features of the chromium oxide epitaxial growth on the (100) β-Ga_2O_3 surface. Fig. 1 presents the optical transmission spectra measured with differential spectrophotometer SPECORD UV-VIS for the β-Ga_2O_3 substrate ($E_g \sim 4.7$ eV) and for a sample with a mist-CVD-grown layer of α-Cr_2O_3 ($E_g \sim 3.1$ eV) $\sim 1\,\mu$m thick. The figure shows that the substrate is transparent in the ultraviolet and visible spectrum ranges, while the chromium oxide layer is transparent only in the visible range. The spectrum of the chromium oxide layer on gallium oxide wafer is similar to that we previously observed for layers grown on sapphire [8] and exhibits optical absorption bands characteristic of chromium oxide. The X-ray diffraction pattern (Fig. 2) obtained on device DRON 8-N with the CuK_α radiation for α-Cr_2O_3/β-Ga_2O_3 demonstrates a series of peaks from the (100) β-Ga_2O_3 substrate and a single peak associated with the α-Cr_2O_3 layer, which we identify as a reflection from the $(11\bar{2}6)$ plane. Note that the layer grown in the same mist-CVD process on a sapphire wafer with the (0001) orientation exhibits two reflections (0006 and 000.12) similar to what was noted in all the studies devoted to growing α-Cr_2O_3 on the basal surface of sapphire. Technological modes did not have a significant impact on the reflection peak $11\bar{2}6$ parameters. This reflection was observed in diffraction patterns of all the α-Cr_2O_3/β-Ga_2O_3 structures grown at 500 and 800 °C. The Table presents measurements of the half-widths at half-maximum ($FWHM_\omega$) of the reflection $11\bar{2}6$ rocking curves obtained on a double-crystal diffractometer. The layered structure was a texture with a fixed orientation of planes $(11\bar{2}6)$ in the direction perpendicular to the surface. Minimal $FWHM_\omega$ was 1.5°. Adding dopants in the process of growth led to the layer structure disordering and transition to the polycrystalline state. Note that along with this a decrease in the layer electrical resistance was observed. The surface morphology of the (100) β-Ga_2O_3 wafer remains smooth after epitaxial deposition of α-Cr_2O_3 (Fig. 3, *a*). Elemental analysis of the α-Cr_2O_3/β-Ga_2O_3 samples performed with a scanning electron microscope indicates that the oxide sample contains only Ga and Cr (Fig. 3, *b*).

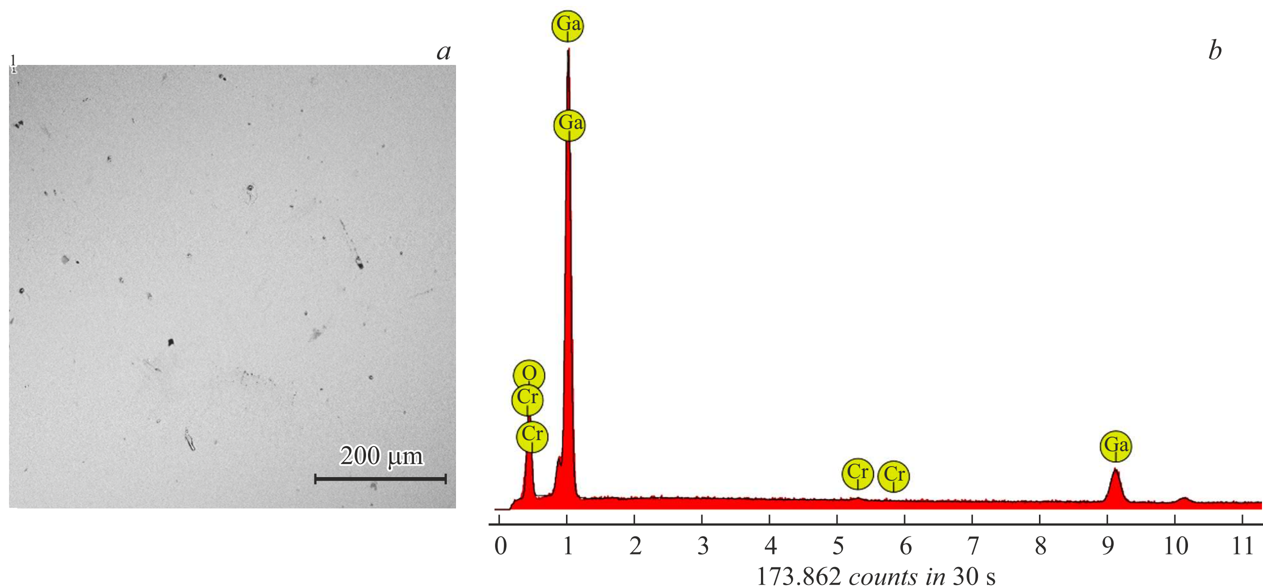

Figure 3. *a* — surface electron image of the α-Cr_2O_3/β-Ga_2O_3 sample grown at 500 °C and annealed at 800 °C; *b* — analysis of its elemental composition.

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Conflict of interests

The authors declare that they have no conflict of interests.

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