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Synthesis of thin single-crystalline α-Cr_2O_3 layers on sapphire substrates by ultrasonic-assisted chemical vapor deposition

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Single-crystalline α-Cr_2O_3 layers were synthesized on a sapphire substrate with a basal orientation in a laboratory reactor using ultrasonic-assisted chemical vapor deposition in the temperature range of 700−850°C. The influence of the growth temperature on the structural quality of the layer was studied by X-ray diffraction. At a growth temperature of 800°C, continuous layers with a thickness of about $1\,\mu$m were obtained. The layers were transparent in the visible region with a slightly greenish tint and showed some light transmission up to wavelengths of ~ 350 nm. The full width at half maximum of the rocking curve for reflection 0006 was ~ 300 arcsec.

Keywords: chromium oxide, CVD epitaxy, wide-bandgap semiconductor.

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Films of p-type semiconductor oxides, such as CuO, NiO, Co_3O_4, α-Ir_2O_3, α-$(Rh,Ga)_2O$, and Cr_2O_3, hold promise for the fabrication of new semiconductor devices [1–4].

In our view, α-Cr_2O_3 stands out in the above list of crystals as remaining thermally stable up to the melting point ($T_m = 2435$°C) and featuring a corundum-type close-packed lattice $R3c$ (N 167), a high density of $5.22\,\mathrm{g\cdot cm^{-3}}$, mechanical strength, and chemical resistance. In addition, it has a high value of $E_g > 3$ eV; the only other oxide from the above list with a similar value is NiO. Another technologically important feature is that the lattice parameters of α-Cr_2O_3 are better suited for epitaxy on sapphire than the parameters of other compounds.

Samples of chromium oxide (α-Cr_2O_3) for studies performed to date have been prepared by hydrothermal synthesis [5]; magnetron sputtering [6,7]; pyrolysis of aerosols [8]; molecular beam epitaxy [9]; pulsed laser deposition [10]; low-temperature carbonyl chemical vapor deposition [11]; and mist CVD epitaxy in a hot-wall reactor (a process similar to ultrasonic chemical vapor epitaxy) with ammonium dichromate, chromium chloride [12], and chromium acetylacetonate [13] used as chromium precursors.

The present study is essentially a report on the results of further development of the last of the listed techniques. The authors of [9] limited themselves to examining the growth of an epitaxial layer in a mist reactor at a temperature of 700°C or lower and, consequently, did not fabricate a layer of a sufficient crystalline quality. The probable reason behind this is that the authors intended to obtain solid solutions of chromium oxide with metastable α-Ga_2O_3, which undergoes a polymorphic transition at a temperature slightly higher than 500°C. The potential of α-Cr_2O_3 used as a buffer for improving the quality of α-Ga_2O_3 layers grown on sapphire has been examined in our earlier studies; layers of chromium oxide with a thickness of $150\,\mu$m have been formed by magnetron deposition with subsequent annealing at $T = 500-800$°C. It has been demonstrated that a α-Cr_2O_3 layer applied beforehand facilitates the formation of a monopolymorphic film of gallium oxide, suppresses the growth of phases with their structure differing from the corundum one, and reduces the density of threading dislocations by a factor of 4 [14].

In the present study, the chromium precursor (chromium(III) tris-acetylacetonate, $Cr(acac)_3$) was synthesized in a slightly different process that was characterized in detail in [15]. A weighted portion of 26.6 g (0.1 mol) chromium(III) chloride hexahydrate ($CrCl_3 \cdot 6H_2O$) was dissolved in a mixture of 200 ml of water and 100 ml of 95%-pure ethanol. Acetylacetone (0.1 mol, 30 g/30.8 ml) was added to the obtained solution, and 0.3 mol (20.4 g/22.5 ml) of a 25% aqueous solution of ammonia were instilled by drops at room temperature under vigorous stirring. The solution was then heated to 60°C, stirred for 5 h, and left at rest for the night. To purify the product, it was dissolved in 300 ml of boiling 95%-pure ethanol, diluted slowly with an equal volume of hot water, and cooled to room temperature under stirring. The product yield was 29 g (83%). $Cr(acac)_3$ was then dissolved in water. The solubility of chromium(III) tris-acetylacetonate in water at 20°C is very low ($\sim 1.87 \cdot 10^{-3}$ mol/l [16]). A 0.1 M solution of hydrochloric acid was used to enhance the solubility of $Cr(acac)_3$. It was determined gravimetrically that the solubility of $Cr(acac)_3$ in this system is $5.7 \cdot 10^{-3}$ mol/l. To prepare the needed solution, 2.0 g of

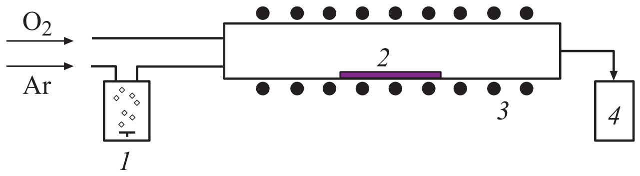

Figure 1. Diagram of the ultrasonic chemical vapor epitaxy (mist CVD) reactor. *1* — Ultrasonic evaporator, *2* — substrate, *3* — furnace, and *4* — bubbler.

$Cr(acac)_3$ (0.006 mol) were introduced slowly into a 0.1 M solution of hydrochloric acid under vigorous stirring. The mixture was stirred for 5–6 h at a temperature of 80°C, introduced into an ultrasonic bath for 30 min, and left at rest for 24–48 h at room temperature for equilibration. If needed, the solution was filtered through filter paper.

Layers were grown in a reactor of a proprietary design for ultrasonic chemical vapor epitaxy (mist CVD) with an ultrasonic radiator operated at 2.4 MHz, which provides vapor droplets 10–100 nm in size [17]. Chromium oxide Cr_2O_3 was synthesized from an aqueous solution of $Cr(acac)_3$ (0.0056 mol/l), which was vaporized and transported from the radiator to a hermetically sealed hot-wall quartz reactor by transport gas (Ar). Oxygen was supplied via the second channel (Fig. 1). The ratio of flows of argon with the CR precursor and oxygen was 10:1. A sapphire substrate was positioned parallel to the gas flow on a special support in the reactor. The growth area was heated by a resistance furnace. Temperature was monitored by a proportional-integral-derivative controller with a thermocouple. Gas was discharged from the reactor through a bubbler with distilled water, which provided the needed excess pressure and accumulated the gas condensate. The substrate temperature was varied within the range of 700–850°C in a series of growth experiments with a duration up to 180 min. The quality of layers was inspected using a DRON X-ray diffractometer in single-crystal and double-crystal geometries with a $\mathrm{Cu}K_{\alpha 1}$ source with an emission wavelength of 1.5406 Å. The layer surface was examined with a Phenom PRO X scanning election microscope (SEM), the optical transparency was monitored with a SPECORD UV-VIS spectrophotometer, and the surface profile was studied using a MarSurf PS 10 profilometer.

The $\theta-2\theta$ X-ray diffraction pattern (Fig. 2) reveals the presence of an epitaxial layer of chromium oxide with a corundum-type crystal structure (α-Cr_2O_3) with its orientation being the same as that of the (0001) α-Al_2O_3 (sapphire) substrate. The FWHM of the rocking curve (FWHM of reflection 0006) is 300 arcsec, which is indicative of a fine structural quality of the obtained layer. The maximum layer thickness estimated by examining a cleaved face of the sample was $\sim 1\,\mu$m. Thus, the mean rate of growth along the normal to the substrate was $0.3\,\mu$m/h. This value is comparable to the mean growth rates of α-Ga_2O_3 in a similar reactor [18] and is slightly lower than the maximum growth rates ($1\,\mu$m/h) achieved in similar experiments [19]. The films grown at 750–800°C were transparent in the visible region with a slightly greenish tint

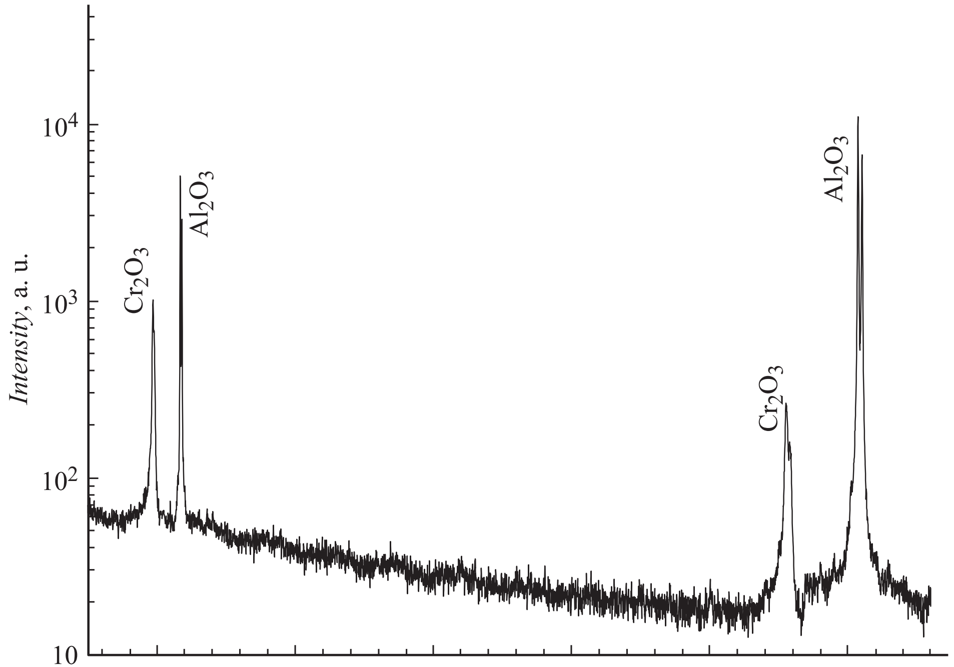

Figure 2. $\theta-2\theta$ X-ray diffraction pattern of a Cr_2O_3 film on the (0001) sapphire substrate.

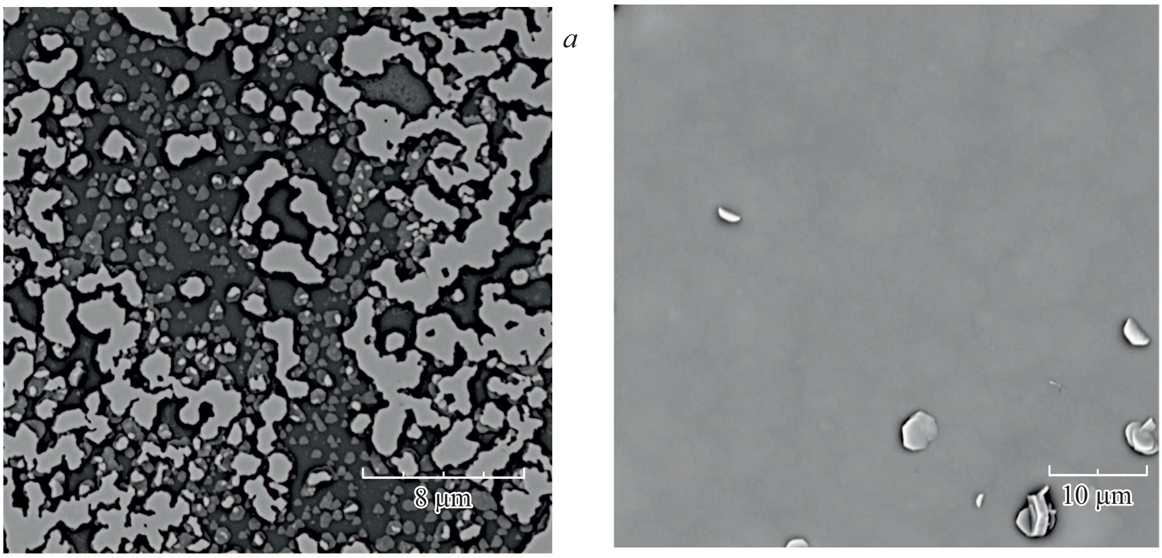

Figure 3. Formation of an epitaxial α-Cr_2O_3 film on the substrate. *a* — Prior to the complete coalescence of islands (growth time, 1 h), *b* — after the formation of a continuous film (growth time, 3 h).

and retained a certain optical transmission up to $\lambda \sim 350$ nm (i.e., up to the α-Cr_2O_3 absorption edge, 3.4 eV [7]).

The surface morphology of an epitaxial α-Cr_2O_3 layer is illustrated in Fig. 3, where two SEM images obtained prior to the complete coalescence of growth islands and after the formation of a continuous film are presented. According to profilometry data, the surface roughness of a continuous film was $R_a = 0.056\,\mu$m. The continuous α-Cr_2O_3 layer grown at 800°C had a high electric resistance (approximately 70 MΩ under the probe).

Continuous epitaxial α-Cr_2O_3 layers with a maximum thickness of approximately $1\,\mu$m were fabricated. The structural and surface quality of these layers is sufficiently high for subsequent epitaxy of oxide semiconductors in the process of formation of a heterophase $p-n$ junction.

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Conflict of interest

The authors declare that they have no conflict of interest.

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