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Fabrication of $\alpha\text{-Ga}_2\text{O}_3\text{:Sn}/\alpha\text{-Cr}_2\text{O}_3/\alpha\text{-Al}_2\text{O}_3$ heterostructure by mist CVD and HVPE

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Abstract

Corundum-structured chromium oxide ($\alpha\text{-Cr}_2\text{O}_3$), exhibiting *p*-type conductivity, is a highly attractive candidate for forming high-quality *p-n* heterojunctions with $\alpha\text{-Ga}_2\text{O}_3$. Two CVD growth techniques were employed in the fabrication of the heterostructure. A ~ 0.2 -micron $\alpha\text{-Cr}_2\text{O}_3$ layer was grown on a (0001) sapphire substrate using mist CVD at 800 °C. It possesses high morphological homogeneity and low roughness, which is acceptable for further epitaxial processes. Subsequently, Sn-doped $\alpha\text{-Ga}_2\text{O}_3$ with a thickness of ~ 1.5 μm was grown on the $\alpha\text{-Cr}_2\text{O}_3$ layer using HVPE at 500 °C. The feasibility of fabricating this heterostructure with the specified layer thickness and acceptable surface morphology using CVD techniques has been demonstrated.

Keywords: Gallium Oxide, Sapphire substrate, Heteroepitaxy, CVD, Mist-CVD, HVPE

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1. Introduction

Gallium oxide is a new-generation semiconductor that opens up horizons in applications in power and high-frequency electronics [1–3]. This promising material outperforms all known commercial semiconductors in terms of electrical, optoelectrical, chemical, and mechanical properties [4]. Its α -polymorph has a corundum-type structure (R3c symmetry). Among the five Ga₂O₃ modifications, it has the largest bandgap ($E_g = 5.3$ eV), along with a high breakdown field ($E_c = 8.5$ MV·cm⁻¹) and dielectric constant ($\epsilon = 10$) [5–7]. By doping gallium oxide with Sn or Si, *n*-type conductivity can be achieved with an electron concentration of up to 10¹⁹ cm⁻³ [8]. However, a method to provide *p*-type conductivity has not yet been found, which is perhaps the biggest drawback of this material, limiting its potential applications.

It is, however, feasible to create a heterojunction of α -Ga₂O₃ with another material owing the same crystal structure while demonstrating *p*-type conductivity [9]. Among the promising candidates, α -Cr₂O₃ stands out as one of the best options. Both share the same rhombohedral structure and have a very low *a*-plane lattice mismatch (0.4%). The latter parameter mismatch is slightly more attractive for α -Ir₂O₃ (0.3%) [10]. Nonetheless, the high cost associated with iridium renders it impractical for practical consideration. Another inexpensive candidate is α -Fe₂O₃, but it has a 1.2% lattice mismatch and a lower optical bandgap (2.3 eV vs. 3.0 eV for α -Cr₂O₃) [11]. To be fair it should be noted, that the lattice mismatch in α -Al₂O₃/ α -Cr₂O₃ pair is high (3.74% [12]), but the double pairing choice is limited.

In our previous work [13], we demonstrated a α -Ga₂O₃/ α -Cr₂O₃/sapphire structure. Our aim was to create a buffer layer of α -Cr₂O₃ to enhance the crystal quality of gallium oxide. The deposition of a 150 nm chromium oxide layer using magnetron deposition, followed by annealing at 500–800 °C, contributed to the growth of corundum α -Ga₂O₃ in a single phase, resulting in a fourfold reduction in threading dislocation density. This experimental evidence confirms the isostructural nature of these oxides and their potential for further research.

Recently, mist-CVD and HVPE have emerged as two CVD techniques of particular interest

for Ga₂O₃ growth [14–17]. Among all vapor-phase methods, only these two methods allow the production of thick layers of gallium oxide [18, 19]. Both techniques offer high growth rates (microns per hour) and simple doping schemes. When employed, they enable the achievement of high crystal perfection along with high-quality surface morphology. Moreover, these methods are cost-effective as long as vacuum setups are not required.

In this paper, we employ mist-CVD and HVPE techniques to fabricate a α -Ga₂O₃/ α -Cr₂O₃/sapphire heterostructure. The primary goal of this work is to determine the fundamental feasibility of growing such a heterostructure using CVD, while achieving the specified layer thickness and maintaining acceptable surface morphology.

2. Experimental

Cr/Ga oxide heterostructures were grown on epi-ready sapphire *c*-plane (0001) substrates. In the first step, a Cr₂O₃ layer was deposited using the mist-CVD technique. We employed a homemade mist-CVD reactor equipped with a 2.4 MHz ultrasonic transducer, which produces droplets with a diameter in the range of 10–100 nm. The growth run lasted for 180 minutes, and the substrate temperature was maintained within a range of 700–850 °C. Detailed descriptions of the precursors and process parameters can be found in [20].

In the second step, a layer of Ga₂O₃ was deposited over the Cr₂O₃ layer using the HVPE method. We also utilized a homemade setup for this process. This reactor is built according to a hot-wall horizontal design and uses gallium chloride (GaCl) and oxygen (O₂) as precursors. The growth rate was approximately 2.4 μ m/h, and the process temperature was set at 500 °C. Additional information regarding the process parameters can be found in [7].

The phase composition of the fabricated heterostructures was characterized by X-ray diffraction (XRD) technique. The Bourevestnik DRON 7 diffractometer with CuK _{α 1} = 1.5406 Å radiation was used. The surface roughness of the Cr₂O₃ layer was measured by Mahr MarSurf PS10 profilometer. The surface morphology of the Ga₂O₃ layer was analyzed using a Phenom ProX scanning electron microscope (SEM) operating in

secondary electron mode. To visualize the cross-section of the heterostructure and ascertain the thickness of the layers, samples were sectioned and examined by SEM.

3. Results and Discussion

The surface morphology of the first layer, which underwent the subsequent epitaxy process, should ideally be as smooth as possible. The visualization of the α -Cr₂O₃ layer's morphology is presented in Fig. 1. It is evident that the surface exhibits a homogeneous relief with no distinct features, except for some spots related to layer defects.

The roughness (r_a) of the α -Cr₂O₃ layer was measured by the profilometer in both directions threefold. The r_a values appeared to be close and the average value ($\bar{r}_a = 24$ nm) and is happened to be low enough for a consequent epitaxy process. The selected profiles of chromium oxide layer surface are shown in Fig. 2.

In the next step, the α -Ga₂O₃ layer was grown using the HVPE method. The surface morphology of this layer is depicted in Fig. 3, where distinct surface features can be observed.

The cross-sectional SEM image of the α -Ga₂O₃/ α -Cr₂O₃/sapphire heterostructure is shown in Fig. 4. The thickness of the α -Ga₂O₃ layer is almost uniform along its lateral direction, measuring approximately 1.5 μ m. Similarly, the α -Cr₂O₃ layer exhibits consistent thickness, albeit at a lower value of about 0.2 μ m.

Analysis of the XRD θ -2 θ curve of α -Ga₂O₃/ α -Cr₂O₃/sapphire heterostructure revealed (000 l)

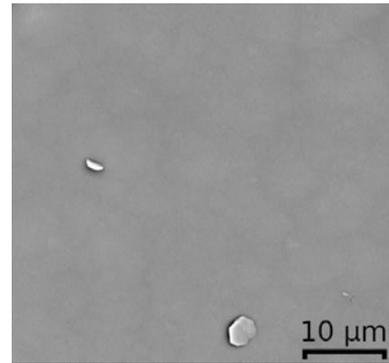


Fig. 1. SEM plan-view image of α -Cr₂O₃ layer grown by mist-CVD

plane reflections for all three phases, plotted in logarithmical scale (see Fig. 5). Namely: for α -Al₂O₃ (0 0 0 6) is at 41.69 deg, (0 0 0 12) is at 90.69 deg; for α -Cr₂O₃ (0 0 0 6) is at 39.8 deg, (0 0 0 12) is at 85.9 deg; for α -Ga₂O₃ (0 0 0 6) is at 40.25 deg, (0 0 0 12) is at 86.96 deg. The angle values for sapphire and gallium oxide both coincide the tabulated ones very well. However, in the case of chromium oxide the experimental values differ significantly from the tabulated values ((0 0 0 6) is at 38.96 deg, (0 0 0 12) is at 83.66 deg). Since both values are shifted towards larger angles, this indicates decrease in lattice parameter of this phase relative tabulated one. One can conclude that the Cr₂O₃ layer, being a buffer one is stressed due to lattice mismatch of the neighbors.

Finally, employing the chromium oxide buffer layer, it was possible to grow homogeneous

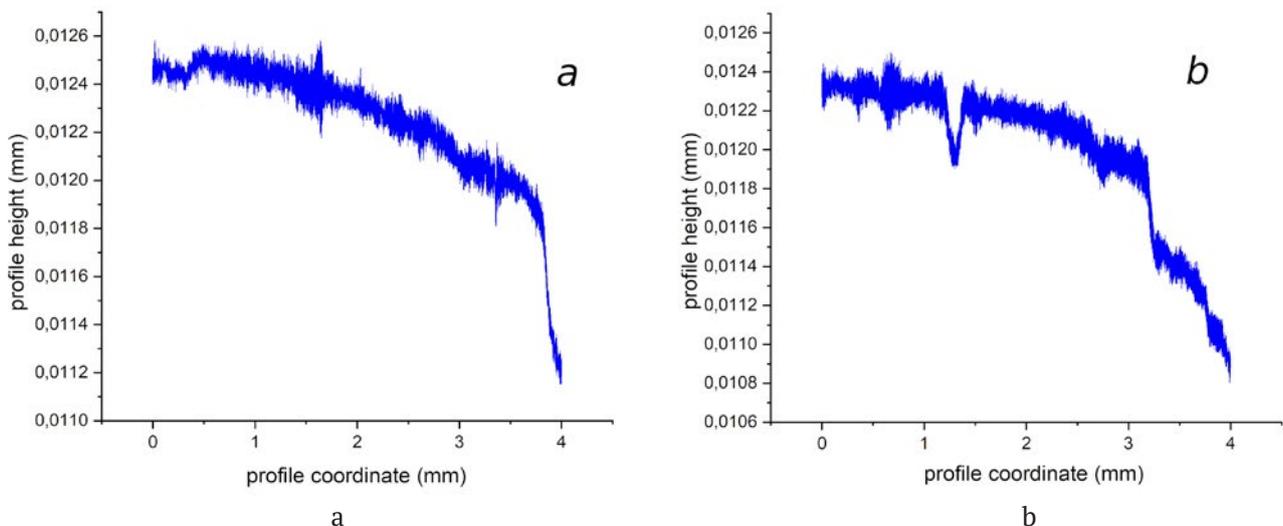


Fig. 2. The α -Cr₂O₃ layer surface relief in both lateral directions (a) OX direction scan, (b) OY direction scan

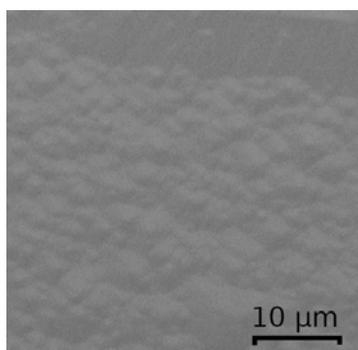


Fig. 3. SEM plan-view image of α -Ga₂O₃ layer grown by HVPE

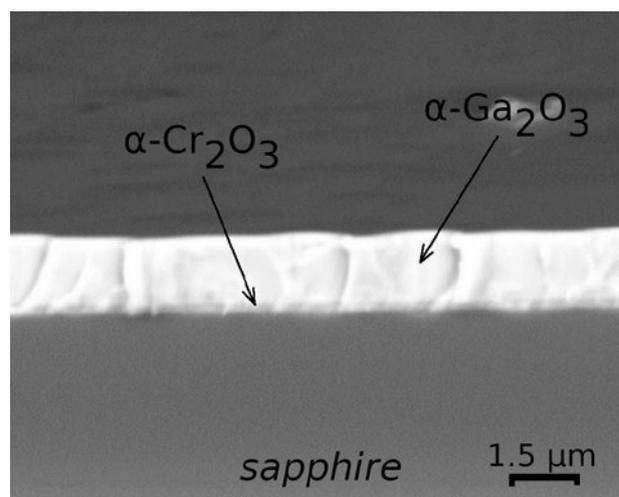


Fig. 4. SEM bird's eye view image of the α -Ga₂O₃/ α -Cr₂O₃/sapphire heterostructure

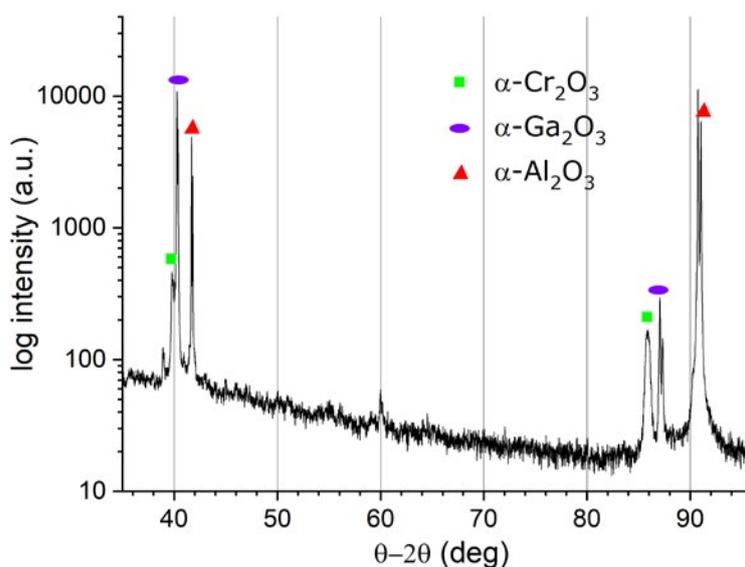


Fig. 5. XRD pattern of α -Ga₂O₃/ α -Cr₂O₃/sapphire heterostructure

1.5 μ m-thick gallium oxide layer with a constant thickness and relatively smooth surface. It is characterized by single-phase structure of relatively high perfection.

4. Conclusions

Thus, we have demonstrated the feasibility of fabricating α -Ga₂O₃/ α -Cr₂O₃/sapphire heterostructures with the specified thicknesses and excellent morphology using CVD techniques. Both mist CVD and HVPE exhibit high growth rates. XRD patterns reveal the absence of any phases other than corundum-like.

Further studies are planned to focus on measuring the electrical parameters of the heterostructure and thinning the sapphire layer. This will allow the creation of a substrate with high thermal conductivity. It is also planned to investigate the possibility of separating the Ga₂O₃ layer from the sapphire substrate to obtain free-standing layers. This will allow the growth of high-quality gallium oxide layers on Cr₂O₃ buffer layer for device applications.

Contribution of the authors

The authors contributed equally to this article.

Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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