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Phase transformations in gallium oxide layers

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The three main crystalline modifications of Ga_2O_3, namely α-phase, ε--phase, and β--phase were grown on sapphire substrates using the hydride vapour phase epitaxy (HVPE) method. The temperatures of the substrates and the values of the precursor fluxes required to obtain each phase exclusively were determined. It was observed that the metastable ε-phase easily transforms into a stable β-phase during annealing. However, the metastable α-phase undergoes an intermediate amorphous phase during annealing, leading to flaking and collapse. This behavior arises from the excessively large increase in density ($\sim 10\%$) during the transformation from α--phase to β--phase, which results in significant elastic stresses and an increase in the height of the phase transition barrier.

Keywords: reconstructive phase transitions, gallium oxide, polymorphs, Raman spectrum.

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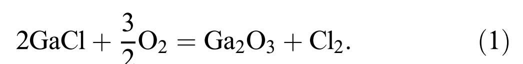
The interest in reconstructive first-order phase transitions in crystalline solids (i.e., transitions accompanied by the breaking of a large number of chemical bonds and the formation of new ones [1,2]) has remained high in the last decades. The change in density and entropy is significant in such phase transitions, which include, e.g., transitions involving ferromagnetic and ferroelectric phases ($BaTiO_3$, $CdTiO_3$, $PbTiO_3$, $PbZrO_3$), metal−semiconductor transitions (VO_2), and transitions between different polymorphic phases. First-order transitions in liquids and amorphous phases have been examined fairly thoroughly, and the corresponding nucleation theory has long been developed [3–6]. However, a similar theory for crystalline solids is still in an embryonic stage [2,7]. That said, an elementary nucleation theory for the simplest cases is available [8], and a quantum-mechanical model relying on the density functional method [9] was constructed for certain transformations (e.g., transitions between the main hexagonal polytypes of silicon carbide 2*H*-SiC, 4*H*-SiC, and 6*H*-SiC). Silicon carbide is one of many semiconductors that have several polymorphic phases differing in their symmetry, density, and other physical parameters. Specifically, gallium oxide (Ga_2O_3) [10–12] stands out among the so-called transparent conductors, which are very relevant now and often turn out to be metal oxides. First, it is a semiconductor with a very large bandgap ($\sim 5\,\mathrm{eV}$); second, it has a very high breakdown voltage ($\sim 8\,\mathrm{MV\cdot cm^{-1}}$); third, it is doped easily, which makes gallium oxide a promising material for micro- and optoelectronics applications. In addition, it is easy to mix with magnetic Cr_2O_3 and, consequently, has potential applications in spintronics. Another important feature of Ga_2O_3 is the existence of several crystalline modifications. The following five main phases of it were identified in reviews [10–12]: stable β-phase with monoclinic structure $C2/m$ and metastable ε-phase with orthorhombic structure $Pna2_1$, α-phase with rhombohedral structure $R\bar{3}c$ (corundum structure), δ-phase with body-centered cubic structure $Ia\bar{3}$, and γ-phase with cubic structure $Fd\bar{3}m$. Although the number of metastable phases is fairly large, they are very hard to synthesize, since the stable β-phase dominates over them in the process of growth. A method for production of three main phases of gallium oxide (namely, stable β-phase, metastable α-phase, and metastable ε-phase) with the use of hydride vapor-phase epitaxy (HVPE) and hybrid 3*C*-SiC/Si substrates at different temperatures has been developed in [13]. In the present study, these three phases were synthesized in a similar fashion, but on sapphire (Al_2O_3), which is crucial for the α-phase that has the same corundum structure found in sapphire. It was found that metastable phases tend to transform into the stable β-phase during annealing. While the ε-phase transforms into the β-phase fairly easily and rapidly, the transformation of the α-phase into the β-phase is very difficult and slow with a film basically undergoing complete destruction in the process (i.e., it detaches from a substrate and crumbles). In the present study, this is attributed to a strong density change in a reconstructive phase transition. A transformation with a significant reduction in density and an increase in volume is accompanied by formidable elastic stresses and, consequently, results in disintegration of a sample.

Standard sapphire substrates with orientation $\langle 0001 \rangle$ were used to grow Ga_2O_3 layers. The following chemical reaction of HVPE of Ga_2O_3 layers was implemented:



$$2\mathrm{GaCl} + \frac{3}{2}\mathrm{O_2} = \mathrm{Ga_2O_3} + \mathrm{Cl_2}. \qquad (1)$$

Gallium chloride was synthesized directly in the source region of the reactor by flowing gaseous hydrogen chloride

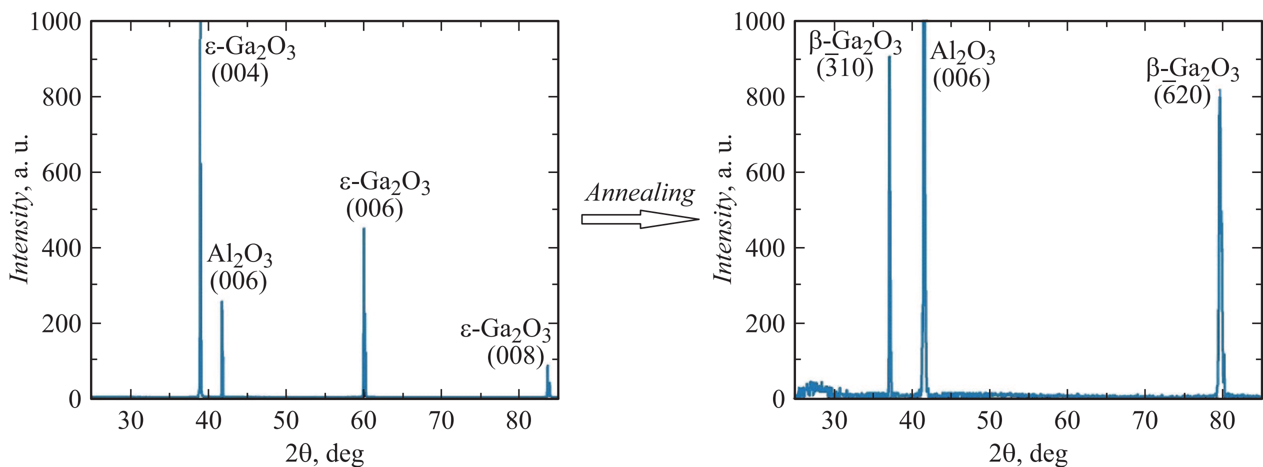


Figure 1. X-ray diffraction pattern of the ε-phase sample before and after 10 min of annealing at 650°C. The ε-Ga_2O_3 film with orientation $\langle 001 \rangle$ transformed into the β-phase with orientation $(\bar{3}10)$ in the course of annealing.

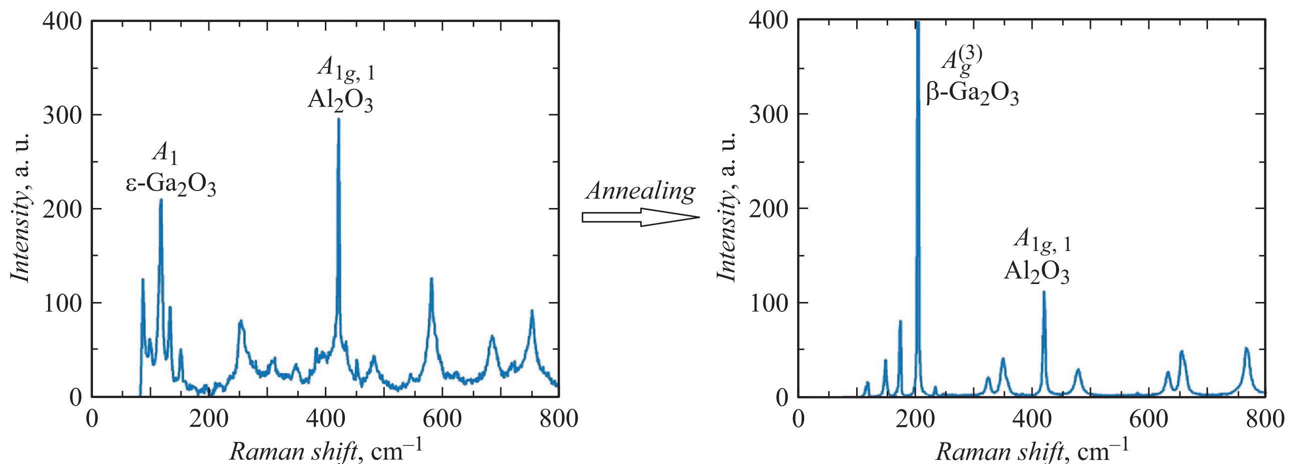


Figure 2. Raman spectrum of the ε-phase sample before and after 10 min of annealing at 650°C. The sole visible line of the Al_2O_3 substrate is marked. All the other lines are decisively identified as belonging to ε- and β-phases [13] (lines of the most interest to us are marked).

(HCl, 99.999%) above metallic gallium (Ga, 99.9999%). The yield of the GaCl synthesis reaction was approximately 85%; the ratio of VI/III components fell within the range of 3−5. With a total gas flow of $\sim 5000\,cm^3$/min, the Ga_2O_3 deposition rate was approximately 0.4−0.5 μm/min at 500°C and 0.8−1.0 μm/min at 1000°C. The deposition time was set within the 2−4 min range so as to fabricate a Ga_2O_3 layer with a thickness of approximately $\sim 2\,\mu$m. The obtained results revealed that different Ga_2O_3 phases are synthesized at different temperatures. At 800−1000°C, Ga_2O_3 was deposited in the stable β-phase (just as in the vast majority of other experiments [14]). At a synthesis temperature of 550−600°C, Ga_2O_3 was deposited exclusively in the metastable ε-phase. At a synthesis temperature of 500−520°C, Ga_2O_3 was deposited exclusively in the metastable α-phase.

Films of Ga_2O_3 in α- and ε-phases were then annealed in vacuum at different temperatures (from 650 to 850°C) for 10−25 min. All the obtained samples were examined via Raman spectroscopy, spectroscopic ellipsometry, and X-ray diffraction both before and after annealing. The results are as follows. At temperatures of 650°C or higher, the metastable ε-phase transforms into the stable β-phase within just 10 min of annealing. Figure 1 presents the X-ray diffraction pattern of the ε-phase sample before and after 10 min of annealing at 650 °C. Figure 2 shows the Raman spectra of the same sample before and after annealing. it is evident that the non-annealed sample was an epitaxial ε-phase Ga_2O_3 film oriented in direction $\langle 001 \rangle$; following annealing, it transformed into an epitaxial β-phase Ga_2O_3 film oriented in direction $(\bar{3}10)$. The Raman spectrum lines also correspond completely to the lines of ε- and β-phases of Ga_2O_3 [13]. Interestingly, the β-phase of Ga_2O_3 grows on sapphire substrates in a different direction (namely, $(\bar{2}01)$) at temperatures of 800−1000°C. Ellipsometric spectra revealed that the ε-phase Ga_2O_3 film

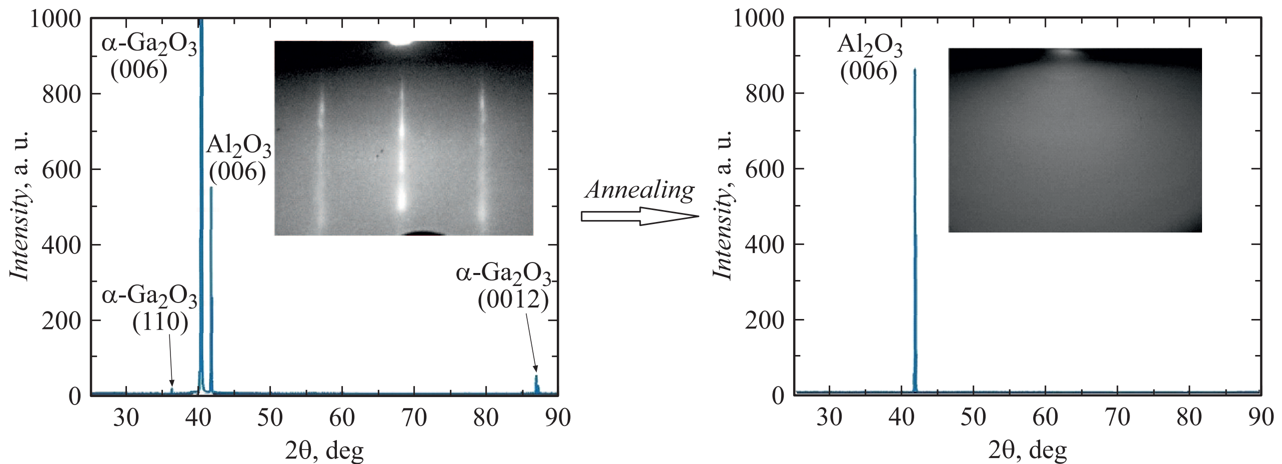


Figure 3. X-ray diffraction pattern of the Ga_2O_3 α-phase sample before and after 15 min of annealing at 750°C (immediately prior to flaking). The high-energy electron diffraction patterns for the same sample before and after annealing are shown in the insets. The α-Ga_2O_3 film with orientation $\langle 001 \rangle$ transformed into an intermediate amorphous phase during annealing (and then flaked away before transforming into the stable β-phase).

had a thickness of 2.55 μm and zero pore density prior to annealing, while the β-phase Ga_2O_3 film after annealing was 2.73 μm in thickness and had a volumetric pore fraction of 4%. Optical microscopic images also revealed a large number of cracks in the annealed film. The following densities of Ga_2O_3 phases were determined via density functional calculations [13]:

$$\rho_\alpha = 6.5\,\mathrm{g/cm^3},\ \rho_\varepsilon = 6.05\,\mathrm{g/cm^3},\ \rho_\beta = 5.9\,\mathrm{g/cm^3}.$$

This implies that the reconstructive transition from the ε-phase to the β-phase is accompanied by a 2.5% increase in volume. In addition, the volume increases by a further 4% as a result of cracking; therefore, the film thickness should rise by 6.5% (i.e., 0.17 μm), and this agrees perfectly with ellipsometric data.

The reconstructive transition from the α-phase to the β-phase of Ga_2O_3 proceeds in an entirely different way. When the metastable α-phase film was annealed at a temperature of 650°C for 25 min, the β-phase did not emerge; i.e., the intensity of X-ray and Raman lines corresponding to the α-phase decreased almost to zero, but no new lines of the β-phase appeared. The film became bumpy and cracked in the process. The film annealed at 750°C for 25 min flaked away and was destroyed completely. At a temperature of 850°C, the film disintegrates approximately within 10 min. The X-ray diffraction patterns of the sample recorded before and after 15 min of annealing at 750°C (i.e., immediately prior to flaking) are shown in Fig. 3. It is evident that the old α-phase vanishes after annealing, but no signs of the new β-phase are seen (only the substrate lines are present). The insets in Fig. 3 show the high-energy electron diffraction patterns for the Ga_2O_3 sample before and after 15 min of annealing at a temperature of 750°C. These patterns were recorded with an EMR-100 electron diffractometer at an electron energy of 50 keV. It can be seen that the epitaxial α-phase was present before annealing and an amorphous phase emerged after annealing. A similar pattern can be seen in the Raman spectrum. All lines of the α-phase were well-pronounced before annealing, and only the sapphire substrate lines remained after annealing. Since the annealed sample was covered with a large number of cracks and its surface became rough (with a roughness parameter on the order of 50 μm) and bumpy, it did not reflect light, making it impossible to perform ellipsometric measurements. It may be concluded that the newly produced phase is completely amorphous and does not contain any appreciable amount of the crystalline β-phase.

Thus, it was demonstrated that reconstructive phase transitions of Ga_2O_3 to the stable and the least dense phase proceed in entirely different ways. While the transition from the ε-phase to the β-phase with a 2.5% density reduction is fairly easy and fast at a temperature of just 650°C (and is accompanied by only mild cracking), the transition from the α-phase to the β-phase with a 10% density reduction proceeds with much more difficulty. Subjected to enormous elastic stresses, the transition reaches only an intermediate amorphous phase, and the sample then disintegrates without transforming into the stable β-phase. It was thus concluded that elastic stresses play a pivotal role in reconstructive phase transitions by raising the nucleation barrier. If the volume enhancement is too significant, the transformation may fail to be completed.

Funding

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Conflict of interest

The authors declare that they have no conflict of interest.

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