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Growth of thick $\varepsilon(\kappa)$-Ga_2O_3 films by halide vapor phase epitaxy

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High crystalline quality epitaxial films of orthorhombic gallium oxide $\varepsilon(\kappa)$-Ga_2O_3 with a thickness of more 20 μm have been grown for the first time using halide vapor phase epitaxy. Sapphire wafers with preliminarily deposited GaN layers were used as substrates. The properties of the produced films are studied by X-ray diffraction and electron microscopy. The results are considered an important step towards obtaining thick layers and quasi-bulk $\varepsilon(\kappa)$-Ga_2O_3 crystals for practical applications in electronics and sensor technology.

Keywords: gallium oxide, halide vapor phase epitaxy, polymorph, X-ray diffraction

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Gallium oxide Ga_2O_3 has recently attracted research attention as a promising ultrawide-gap semiconductor material. Its energy gap ($E_g = 4.7-5.3$ eV) Ga_2O_3 is wider than the one of common wide-gap semiconductors, such as GaN (3.4 eV) and SiC (3.0 eV). Gallium oxide may find application in deep-UV optoelectronic devices, solar-blind radiation detectors, and high-power and high-voltage instruments.

Gallium oxide forms several polymorphic modifications (α, β-, γ-, δ-, and $\varepsilon(\kappa)$-phases). The most thermodynamically stable of them is β-Ga_2O_3 with a monoclinic crystal lattice. The majority of studies are focused on β-Ga_2O_3, since this polymorphic phase may be obtained in the form of both bulk single crystals and thin epitaxial films. However, the crystal structure of β-Ga_2O_3 is characterized by a low degree of symmetry, which translates into a well-pronounced anisotropy of physical properties. Single crystals and β-Ga_2O_3 epitaxial films tend to crack along the cleavage planes, creating significant challenges in device fabrication.

The interest in other polymorphic phases of Ga_2O_3 (especially in metastable α- and ε-Ga_2O_3 phases, which can be obtained by epitaxial growth on oriented substrates) has been on the rise in recent years. Since these polymorphic phases feature a crystal structure with a higher degree of symmetry and a less pronounced anisotropy of physical properties, they are better suited for device applications than β-Ga_2O_3. In contrast to other polymorphic modifications, ε-Ga_2O_3 is a ferroelectric with a relatively strong spontaneous polarization [1,2]. These properties of ε-Ga_2O_3 can be used to fabricate heterostructures with a two-dimensional electron gas and high-power switching devices with high mobility [3].

Phase-pure ε-Ga_2O_3 thin films have been produced for the first time in 2015 by halide vapor phase epitaxy (HVPE) on GaN, AlN, and β-Ga_2O_3 (201) substrates [4]. In later studies, ε-Ga_2O_3 films have also been synthesized by metal organic chemical vapor deposition (MOCVD) [5], mist CVD [6], molecular beam epitaxy [7], and pulsed laser deposition [8]. The growth of ε-Ga_2O_3 on various crystal substrates, such as GaN, AlN, SiC, ZnO, α-Al_2O_3, β-Ga_2O_3, MgO, yttria-stabilized zirconia, etc., has been reported. It should be noted that substrates with a hexagonal crystal structure (e.g., sapphire substrates with a thin GaN or AlN layer) are the best for stabilizing the ε phase.

It has been assumed in early studies [9] that ε-Ga_2O_3 features a hexagonal crystal structure with the space group $P6_3mc$. However, a detailed examination of the microstructure with a high-resolution transmission electron microscopy revealed that ε-Ga_2O_3 is not a standalone phase, but rather a combination of nanosized domains with an orthorhombic crystal structure similar to κ-Al_2O_3 with the space symmetry group $Pna2_1$ [10]. Depending on the domain size and the spatial resolution of the characterization technique, ε-Ga_2O_3 can exhibit either hexagonal (ε) or orthorhombic (κ) symmetry [11]. Therefore, a compound designation ($\varepsilon(\kappa)$-Ga_2O_3) is used hereinbelow.

The halide vapor phase epitaxy technique is characterized by high growth rates (several tens of micrometers per hour [4,12]), which make it most suited for the fabrication of thick layers and quasi-bulk crystals of metastable polymorphic Ga_2O_3 phases. In addition, the presence of chlorine appears to be essential for the stabilization of metastable polymorphic Ga_2O_3 modifications [13].

We have already reported on the fabrication of $\varepsilon(\kappa)$-Ga_2O_3 layers with a thickness up to 5 μm on 2H-GaN, 4H-SiC, and smooth and patterned sapphire substrates [14]. In the present study, the thickness of fabricated $\varepsilon(\kappa)$-Ga_2O_3 layers was increased to more than 20 μm.

Films of Ga_2O_3 were grown by halide vapor phase epitaxy in a horizontal quartz reactor with hot walls. Patterned (0001) sapphire wafers with a predeposited gallium nitride (GaN) buffer layer were used as substrates. This layer was synthesized by MOCVD and had a thickness of $\sim 3-4$ μm. Complete leveling off of protrusions on surface of the patterned sapphire substrate was thus achieved, and

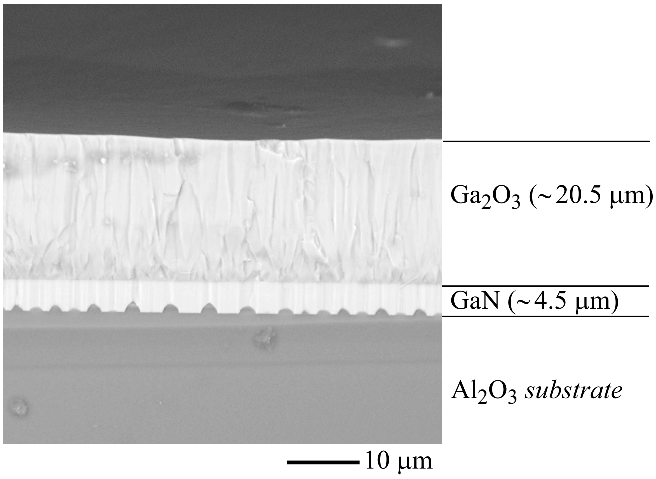

Figure 1. Cross-sectional SEM image of cleaved Ga_2O_3 film on a patterned sapphire substrate with a GaN underlayer.

a planar GaN layer was formed. Gaseous oxygen (O_2) and gallium chloride (GaCl) were used as oxygen and gallium precursors. Gallium chloride vapor was produced in the reactor by flowing gaseous hydrogen chloride (HCl, 99.999%) above a boat with metallic gallium (99.9999%). The flow rate of HCl through the Ga source and the oxygen flow rate were 100 and 300 sccm, respectively. High-purity argon was used as a carrier gas. The deposition of Ga_2O_3 films was performed at in the temperature range of 530−630°C under atmospheric pressure. The crystal structure and the crystalline quality of Ga_2O_3 films were characterized by X-ray diffraction (XRD) with $CuK_{\alpha 1}$ ($\lambda = 1.5405$ Å) radiation. The thickness of Ga_2O_3 films was measured by cross-sectional optical and scanning electron microscopy.

Scanning electron microscopy (SEM) images revealed that the deposited $\varepsilon(\kappa)$-Ga_2O_3 films are uniform and have a planar surface (see Fig. 1). The thickness of films measured on the cleaved samples samples was $1-20\,\mu$m.

Figure 2 shows the typical XRD pattern of a synthesized Ga_2O_3 film. The diffraction peaks at $2\theta = 19.1$, 38.8, 59.8, and 83.2° can be identified as reflections (002), (004), (006), and (008) from $\varepsilon(\kappa)$-Ga_2O_3. Intense peaks from the sapphire substrate and the GaN underlayer are also seen. The weak diffraction peak at $2\theta = 40.9°$ can be identified as reflection (006) of α-Ga_2O_3. Since no diffraction peaks were observed at other positions, it is fair to assume that the films consisted primarily of a pure $\varepsilon(\kappa)$-Ga_2O_3 phase (with an insignificant addition of α-Ga_2O_3).

The crystalline quality of $\varepsilon(\kappa)$-Ga_2O_3 films was determined by measuring the full width at half maximum (FWHM) of X-ray rocking curves for the (006) reflection. Compared to other polymorphic modifications (e.g., α- and β-Ga_2O_3), $\varepsilon(\kappa)$-Ga_2O_3 films feature a lower degree of structural perfection and are characterized by significantly higher FWHM values of rocking curves. In the majority of studies, the FWHM of X-ray rocking curves is greater than 10 arcmin [4,5,12,15], which corresponds to a density of threading dislocations on the order of $10^{10}\,cm^{-2}$. The FWHM of the X-ray rocking curve of the (006) reflection for the $\varepsilon(\kappa)$-Ga_2O_3 films obtained in the present study varied from 4 to 20 arcmin. Figure 3 presents the dependence of the X-ray rocking curve FWHM for the (006) reflection on the $\varepsilon(\kappa)$-Ga_2O_3 layer thickness. It can be seen that the

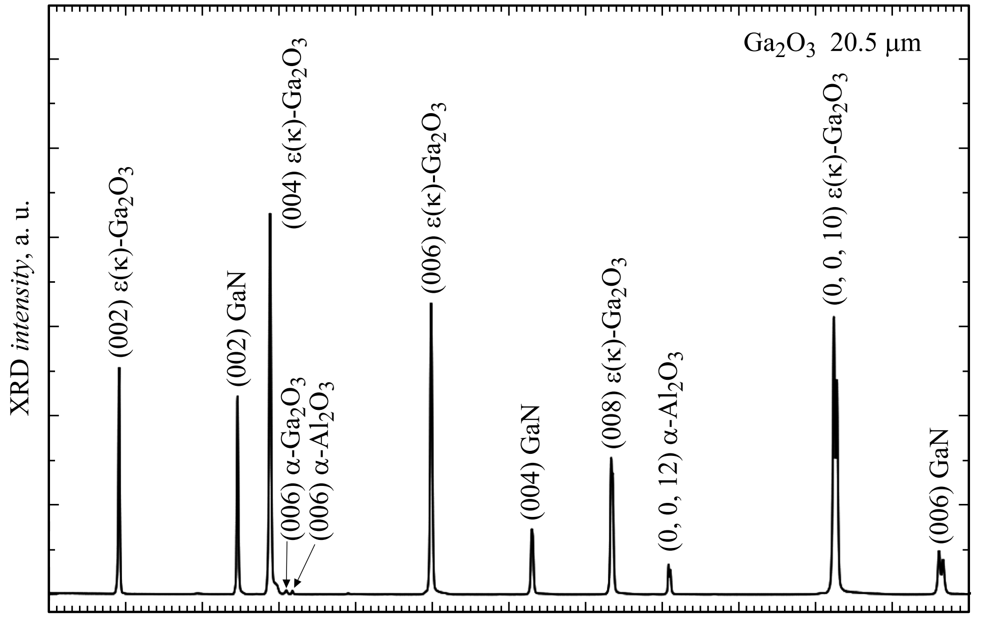

Figure 2. X-ray diffraction pattern of a Ga_2O_3 layer on a patterned sapphire substrate with a GaN underlayer.

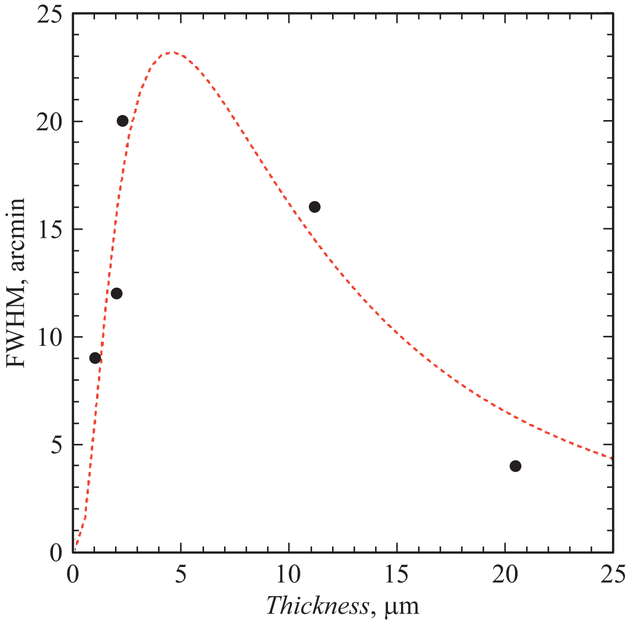

Figure 3. Dependence of the X-ray rocking curve FWHM for the (006) reflection of $\varepsilon(\kappa)$-Ga_2O_3 on the Ga_2O_3 layer thickness.

FWHM value increases with layer thickness up to $\sim 5\,\mu$m; however, as the thickness grows further, the rocking curves get more narrow (i.e., the degree of crystalline perfection of $\varepsilon(\kappa)$-Ga_2O_3 increases). The narrowest rocking curve (FWHM = 4 arcmin) corresponded to the thickest sample with the $\varepsilon(\kappa)$-Ga_2O_3 layer thickness of 20.5 μm.

Thus, thick single-phase $\varepsilon(\kappa)$-Ga_2O_3 layers with to 20.5 μm thick were synthesized by halide vapor phase epitaxy. The full width at half maximum of the X-ray rocking curve for the (006) reflection was 4 arcmin, which is presently a record low. The observed increase in the degree of structural perfection in thicker layers is indicative of the viability of application of halide vapor phase epitaxy in synthesis of thick high-quality $\varepsilon(\kappa)$-Ga_2O_3 layers that may be used to form heterostructures or electronic and optoelectronic instruments and sensors.

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Conflict of interest

The authors declare that they have no conflict of interest.

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