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Formation of various phases of gallium oxide films depending on substrate planes and deposition gases

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ABSTRACT

The crystal phases and orientations of Ga_2O_3 thin films were investigated by RF magnetron sputtering on sapphire C-planes, sapphire A-planes, and Si(100) substrates either in an O_2 or H_2O vapor ambient. When deposited under O_2 gas flow, $(\bar{2}01)$-oriented β-Ga_2O_3 grew on sapphire C-planes at 300 °C for both as-crystallization and solid-phase crystallization. In contrast, (110)-oriented α-Ga_2O_3 grew on sapphire A-planes above 600 °C. Randomly-oriented polycrystalline β-Ga_2O_3 was formed on Si(100) substrates. These experimental results indicate that while a high temperature is needed to form β-Ga_2O_3, the activation barrier of nucleation is greatly reduced by hexagonally packed oxygen atoms on sapphire C-planes. Nucleation and/or crystallization on sapphire A-planes require higher temperatures probably because of sparse surface atoms. Nevertheless, pseudomorphic growth of α-Ga_2O_3 having the same corundum structure is selected due to the template effect of the substrate at elevated temperatures. Deposition with H_2O severely decelerated crystallization and promoted nucleation of γ-Ga_2O_3. Preferentially (311)-oriented γ-Ga_2O_3 was obtained on sapphire C-planes. While pseudomorphic growth of α-Ga_2O_3 occurred on sapphire A-planes above 800 °C, small γ-Ga_2O_3 crystallites coexisted with them. Conversion between the phases was not observed even at 800 °C, reflecting a high activation barrier for rearrangement of atoms that constitute crystalline lattices.

1. Introduction

Ga_2O_3 has recently been attracting considerable attention in oxide electronics. Although an undoped Ga_2O_3 film exhibits n-type electric conduction [1,2], it is basically an insulator having the widest bandgap (5 eV) of all solid-state oxides. This is the primary reason Ga_2O_3 has been less utilized in electronic devices. Since the successful growth of large single crystals [3–5], however, Ga_2O_3 has come to be recognized as an emerging material that it is suitable for power devices. To date, Ga_2O_3 single crystals have been available from suppliers as epitaxial substrates [6], which can be alternatively used instead of sapphire, SiC, or GaN substrates. Demonstrating the feasibility of Sn-doped Ga_2O_3 as an n-type semiconductor [7] has opened up the device research field regarding Ga_2O_3. The main target devices under development include field-effect transistors (FETs) [6], UV photo detectors [8,9], and power devices that are robust under high temperature and high voltage environments, thus achieving low energy consumption. Other applications that are expected for Ga_2O_3 are in phosphors [10], gas sensors [11–13], and catalysts [14,15].

The seminal paper presented by Roy et al. [16] documented the crystal polymorphs of Ga_2O_3. Starting from Gallia gel (GaO_2H), they synthesized five isomorphic structures: α-Ga_2O_3, β-Ga_2O_3, γ-Ga_2O_3, δ-Ga_2O_3, and ε-Ga_2O_3. Of these, α-Ga_2O_3, β-Ga_2O_3, and γ-Ga_2O_3, are compounds that could be well reproduced by those who followed. In particular, β-Ga_2O_3 [17,18] is known to be the stablest phase that can be converted from other phases through annealing above 900 °C. Various attempts have been devoted to produce electronic devices based on β-Ga_2O_3. α-Ga_2O_3 is the second stablest phase obtained after 12 h of annealing of GaO_2H at 500 °C. Rapid thermal annealing of Ga_2OH at lower temperatures of 400–500 °C yields γ-Ga_2O_3, which is known to be a metastable low-temperature phase. Sinha et al. [19] demonstrated the sequential conversion of crystal forms during the course of annealing sol–gel derived films. The crystalline phases changed into a mixture of GaO_2H and α-Ga_2O_3 at 400 °C, pure α-Ga_2O_3 at 500 °C, a mixture of α-Ga_2O_3 and β-Ga_2O_3 at 600 °C, and pure β-Ga_2O_3 at 700 °C. Similar structures for polymorphs are known for alumina, where α-Al_2O_3, β-Al_2O_3, and γ-Al_2O_3 are the major phases.

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These phases are relevant to bulk crystals as well as nano- and micro-crystallites. The crystalline phase in two-dimensional Ga_2O_3 films terminated with single crystal substrates is strongly affected by the atomic arrangement of the substrates, i.e., the stability and energetics are altered from those of bulk crystals. Most papers that have been published so far have dealt with β-Ga_2O_3 grown on sapphire C-plane surfaces. The employed deposition techniques include pulsed-laser deposition (PLD) [20–22], molecular beam epitaxy (MBE) [23–25], metal-organic chemical vapor deposition (MOCVD) [26–28], sol–gel derived growth [29], and RF magnetron sputtering [30]. However, exceptional results were reported with Mist-CVD, where α-Ga_2O_3 grew on sapphire C-planes [31,32]. Although the source gas is common to those utilized in conventional CVD, Mist-CVD is characterized by the method by which it supplies precursors; they are vaporized with H_2O in the form of mist, which then reacts with the surface of the growing film. Furthermore, we should note that Roy's phase diagram assumes water atmosphere during crystal growth since $Ga_2O_3 \cdot H_2O$ (GaO_2H) is used as the starting substance. Nucleation in the presence of H_2O could be a prerequisite condition to obtain α-Ga_2O_3 [15,31,32]. Similarly, doping with aluminum [33] or cobalt [34] favored the formation of α-Ga_2O_3.

There have been vary few papers reporting Ga_2O_3 crystal growth on substrates other than sapphire C-planes. When sapphire A-planes were employed as substrates, β-Ga_2O_3 was produced with MBE [25]. Polycrystalline β-Ga_2O_3 was formed on Si(100) substrates [12]. γ-Ga_2O_3 has been demonstrated to be stabilized by using spinel $MgAl_2O_4$(100) substrates [35] or doping it with manganese [36]. Such variance in the experimental results suggests that the crystal phase is affected by the choice of the substrate and impurities because of slight differences in the formation energies of α-Ga_2O_3, β-Ga_2O_3, and γ-Ga_2O_3. Lack of information about crystalline phases on surfaces other than sapphire C-plane urges systematic studies by using various substrate planes. It is thus inferred that high temperature is not the only factor for β-Ga_2O_3 being selected. Against this background, we have investigated the crystal phases of Ga_2O_3 films deposited on sapphire C-planes (Al_2O_3(0001)), sapphire A-planes ($Al_2O_3(11\bar{2}0)$), and Si(100) substrates. We employed RF magnetron sputtering as the standard technique to form oxide thin films. Deposition was carried out under an O_2 or H_2O vapor gas flow. Sputtering with H_2O realizes situation similar to that of solution derived growth. We present the factors that determine the crystal phases and orientations based on the experimental results.

2. Experimental details

Ga_2O_3 films were deposited by RF magnetron sputtering from a 2-inch Ga_2O_3 target. The target-substrate distance was 10 cm and the RF power was 60 W. Argon was used as the sputtering gas at a partial pressure of 9.8×10^{-2} Pa, and either O_2 or H_2O gas was additionally fed into the sputtering chamber to supplement oxygen atoms that were to be incorporated into the Ga_2O_3 films. We confirmed that neither the crystalline phases nor crystallographic orientations of Ga_2O_3 films changed within an O_2 gas pressure range between 1 and 3×10^{-2} Pa. While the deposition rate did not depend on substrate temperature, it was considerably affected by O_2 partial pressure because of poisoning of the target surface with oxygen. The O_2 gas pressure for the samples treated in this research was fixed at 2.6×10^{-2} Pa and the deposition time was adjusted between 120 and 130 min to obtain films with a common thickness of 173 nm. For deposition under H_2O gas flow, a stainless bottle filled with water was connected to the deposition chamber through a variable leak valve. H_2O partial pressure was fixed at 3×10^{-2} Pa. The deposition time was 120 min, which yielded 260 nm-thick films. The film thicknesses were evaluated from interference fringes that appeared in the optical transmittance spectra of films deposited on transparent sapphire or glass substrates. Two-inch sapphire C-planes, sapphire A-planes, as well as four-inch Si(100) wafers were used as substrates. The crystallization mode depended on the annealing sequence. One mode was crystallization during sputter-deposition at elevated temperatures (as-crystallization), and another was solid-phase crystallization driven by 1 h of vacuum annealing of amorphous Ga_2O_3 films that had been deposited at room temperature (RT). In this case, the samples were placed in a furnace and heated with a lamp heater. The temperature increased at a rate of 20 Ks^{-1}, and maintained at the present temperature for 1 h. After the annealing was stopped, the sample was cooled down until the temperature reached RT. The atmospheric temperature at the center of the furnace was measured with a thermocouple after the temperature had stabilized at the preset annealing temperature. The thermocouple value was certainly the same as the real temperature of the substrate. When crystallized during sputter deposition, the temperature of the substrate at the backside was monitored with a thermocouple. The real temperature at the front side of the substrate differed from the thermocouple values. The main factor reducing the temperature was radiative heat dissipating into the vacuum and the main factor increasing the temperature was bombardment by the RF magnetron plasma. We determined the real surface temperature from the calibration curve taken in advance.

All deposited Ga_2O_3 films appeared optically smooth. The crystal structures of Ga_2O_3 films were analyzed with X-ray diffraction (Rigaku, RINT 1500) under a Bragg-Brentano configuration and a CuKα emission line was used as the primary X-ray beam. Grazing-incidence XRD (GIXRD) patterns were also measured to judge the crystal quality and identify small crystallites that failed to be detected in the θ/2θ-scan XRD pattern. X-rays were incident along azimuthal direction of $[11\bar{2}0]$ on sapphire C-plane, $[1\bar{1}00]$ on sapphire A-plane, and [100] on Si(100). The incident angle ω was 1.5°. For simplicity, we designate a diffraction peak of α-Ga_2O_3(*klm*) simply as α(*klm*), and similar notations for β(*klm*) and γ(*klm*) are used for β-Ga_2O_3(*klm*) and γ-Ga_2O_3(*klm*). Since all XRD and GIXRD patterns discussed in this paper were measured under exactly the same conditions, their diffraction intensities could be compared. Optical transmittance spectra were measured with a spectrophotometer (Shimadzu, UV-3100) for Ga_2O_3 films deposited on double-side polished sapphire C-plane substrates or on transparent silica glass substrates.

3. Results

3.1. Ga_2O_3 films deposited on sapphire C-planes under O_2 gas flow

Fig. 1(a) depicts XRD patterns of Ga_2O_3 films crystallized during deposition on sapphire C-planes under flowing O_2 gas. Diffraction peaks of β($\bar{2}01$), β($\bar{4}02$), β($\bar{6}03$), and β($\bar{8}04$) appeared for deposition temperatures between 300 and 500 °C. These ($\bar{2}01$)-series peaks appearing with comparable intensities are characteristic of β-Ga_2O_3, as has been reported in the literature [20,23,25]. It is worth noting that crystallization occurred even at 300 °C, which is lower than the lowest crystallization temperature on sapphire C-planes reported so far. Crystallization at such low temperatures means that the crystallization was facilitated by the epitaxial template effect of the sapphire C-plane. Irradiation with RF plasma achieved effectively high-temperature conditions, which may have assisted nucleation by promoting the migration of surface atoms. While the corresponding GIXRD patterns in Fig. 1(b) have diffraction peaks that belong to β-Ga_2O_3, their peak intensities are less than 100 counts, which indicate a very small volume of misoriented domains.