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Influence of Oxygen Pressure on Growth of Si-Doped β-(Al,Ga)2O3 Thin Films on c-Sapphire Substrates by Pulsed Laser Deposition

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Ga2O3 is a deep-UV transparent semiconducting oxide being interesting for solar-blind photo detectors e.g. for flame or missile plume detection. The bandgap of about 4.9 eV can be increased by alloying with Al2O3. We have investigated β-(AlGa)2O3 thin films grown by pulsed laser deposition (PLD) on (00.1) Al2O3 with regard to the influence of the growth parameters such as growth temperature (Tg) and oxygen partial pressure (p(O2)) on the structural, optical and electrical properties of the samples. The thin films have (201) orientation and the cation incorporation strongly depends on the deposition parameters. At a given Tg, the incorporation of Al is favored for lower p(O2) due to higher dissociation energy of the Al-O bond compared to the Ga-O bond. At a given p(O2), the incorporation of Al is favored for higher Tg due to desorption of gallium suboxides during growth.

The samples investigated in this study were grown by pulsed laser deposition (PLD) on (00.1) Al2O3. The ceramic targets for PLD consist of Ga2O3 with 8.8 at.% Al2O3 and were additionally doped with different amounts of Sn, Si or Ge using a 1 MeV Tandem accelerator from NEC. For each sample different implantation energies, for Si, 36, 160 and 600 keV and with fluencies of 1.5 × 1015, 6 × 1013, and 1.5 × 1014 cm−2, respectively, were used to obtain a homogeneous implantation profile. For Sn implanted samples we applied 600 keV

Table I. Range of growth temperature Tg, oxygen partial pressure p(O2) and cation composition of the used PLD targets.

| Target: Ga2O3 + 8.8 at.% Al2O3 + | Growth parameters: | p(O2) in mbar |
|--------------------------------|-------------------|--------------|
| 0.2–4.4 at% SiO2                | Tg in °C           | 3 × 10−4–0.04|
| 0.6 at% SnO2                   |                   | 3 × 10−4–0.024|
| 0.9–4 at% GeO2                 |                   | 3 × 10−4–0.02|

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and 2 MeV and with doses of $5 \times 10^{13}$ and $1 \times 10^{14}$ cm$^{-2}$. To activate the implanted Si and Sn, the samples were annealed at approximately 840°C for one hour in nitrogen ambient. Thin film properties as the alloy composition, structural, optical and electrical properties were investigated by means of energy-dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD), atomic force microscopy (AFM), and Hall effect measurements. The respective bandgap energies $E_g$ and layer thicknesses $d$ were determined by transmission measurements. By extrapolation of $(\alpha h \nu)^2$ vs. photon energy to zero the bandgap energies were estimated and $d$ can be calculated from observable layer thickness oscillations using a refractive index of $n \approx 2.21$. There, $\alpha$ describes the absorption coefficient, $h$ the Planck constant and $\nu$ the wave frequency. For the transport measurements, ohmic contacts, consisting of 30 nm thick layers of titanium, aluminum and gold (Ti/Al/Au), respectively, were thermally evaporated on the corners of the square samples through a shadow mask. Subsequently, these contacts were annealed at 500°C for 10 minutes in a nitrogen ambient.

Results and Discussion

The influence of the oxygen pressure during growth will be discussed in the following section based on a growth series deposited at a growth temperature of 670°C. The used target consists of 86.8 at.% Ga$_2$O$_3$ + 8.8 at.% Al$_2$O$_3$ + 4.4 at.% SiO$_2$ and the oxygen pressure was varied in the range from 0.04 to $3 \times 10^{-4}$ mbar. XRD patterns, shown in Figure 1, indicate a strong influence of $p(O_2)$ on the crystallinity of the samples. The peak appearing at $2\theta = 41.68^\circ$ can be assigned to reflections on the (00.6) plane of the c-plane sapphire substrate. The remaining visible reflection peaks belong to monoclinic gallium oxide. For Ga$_2$O$_3$, For $p(O_2) \leq 0.002$ mbar the thin films grow only in [-201] direction and show reflection peaks at 20 angles of 18.9°, 38.4°, and 59.2° corresponding to reflections at the (-201) lattice planes. Zhang et al. and Wang et al. already reported that $\beta-(Al,Ga)$$_2$O$_3$ thin films on sapphire substrates grow in [-201]-direction$^{18,22}$ as it is the case for binary Ga$_2$O$_3$. Nakagomi and Kokubun recognized, that the order of oxygen atoms of the (001) plane of c-sapphire and the corresponding (-201) plane of $\beta$-Ga$_2$O$_3$ is equal$^{23}$ leading to a minor mismatch between both lattice planes. For growth pressure between 0.006 and 0.016 mbar additionally peaks at 30.4°, 58.3° and 64.7° occur and correspond to reflections at the (-401)-, (-313)- and (-204)-planes, respectively. Further reflection peaks at $2\theta = 29.8^\circ$, 44.2°, 45.3°, and 60° are visible for $p(O_2) = 0.024 - 0.04$ mbar and corresponds to the (400)-, (601)-, (600)-, and (113)-planes.

As the oxygen pressure in the PLD chamber increases, the kinetic energy of the atomic and molecular species arriving at the substrate decreases. The resulting smaller diffusion length leads to the formation of smaller grains, increasing the probability that some of these grains grow in an orientation different from (-201). This effect is in contrast to many other oxide film systems crystallizing in the higher symmetry cubic or hexagonal structure.$^{24}$ The correlation of oxygen pressure and crystal growth was reported by Müller et al., who observed for binary Ga$_2$O$_3$ similar behavior.$^{12}$

Figure 2a shows the calculated growth rates ($r = d/\#\text{pulses}$), bandgap energies and aluminum concentration $x_{Al}$ in dependence on the logarithmic oxygen partial pressure $p(O_2)$. The gray shaded area indicates the $p(O_2)$ regime where desorption is essential. (b) Optical transmittance spectra for oxygen pressures of $p_1 = 0.04$ mbar, $p_2 = 0.002$ mbar, $p_3 = 0.001$ mbar, and $p_4 = 3 \times 10^{-4}$ mbar.
energies were calculated from the optical transmittance spectra and are shown for four different oxygen pressures in Fig. 2b. In Fig. 2a a division into two growth regimes \((p(O_2) \geq 0.016 \text{ mbar} \text{ and } p(O_2) < 0.016 \text{ mbar})\) is recognizable. For \(p(O_2) \geq 0.016 \text{ mbar}\) similar growth rates of 32.5 to 37 pm/pulse, bandgap energies of approximately 5.05 eV and an aluminum content ranging between 0.06 and 0.08 were observed, as well. Below an oxygen pressure of 0.016 mbar the growth rate decreases with decreasing growth pressure up to a value of 12 pm/pulse for \(3 \times 10^{-4} \text{ mbar}\). Simultaneously, the bandgap energies and aluminum contents increases up to values of \(E_g = 5.7 \text{ eV}\) and \(x_{Al} = 0.25\). The influence of the oxygen pressure on the cation composition is illustrated in Figure 3a and show, that with decreasing growth pressure the gallium (aluminum) content \(x_{Ga} (x_{Al})\) decreases (increases) for a given growth temperature of 670 °C. The sum of all incorporated cations is always 1 and the silicon proportion ranges between 0.03 and 0.07.

For oxygen pressures between 0.04 and 0.016 mbar a nearly stoichiometric transfer of the Ga, Al and Si atoms from target to layer is observed and results in similar growth rates and bandgaps (see Fig. 2). In the oxygen regime below 0.016 mbar, aluminum atoms are preferentially incorporated, because of the higher dissociation energy of the Al-O bond compared to the Ga-O bond.\(^{15}\) Further, gallium forms volatile sub-oxides being desorbed. As a result, considerably lower amounts of Ga are incorporated into the layers as seen in Figure 3a. The higher aluminum content leads to the observed bandgap increase and the desorption of gallium sub-oxides leads to lower growth rates. Similar desorption processes were reported for molecular beam epitaxial growth of In\(_2\)O\(_3\), Ga\(_2\)O\(_3\) and (In\(_{x}\)Ga\(_{1-x}\))\(_2\)O\(_3\) thin films by Vogt and Bierwagen.\(^{26–28}\) Since the desorption is a temperature dependent process, we investigated the growth rates of samples deposited at three different oxygen pressures (0.006, 0.001 and \(3 \times 10^{-4} \text{ mbar}\)) and various growth temperatures (from 400 to 670 °C). For deposition of these sample series we used a target consisting of Ga\(_2\)O\(_3\) + 8.8 at.% Al\(_2\)O\(_3\) + 0.6 at.% SnO\(_2\). The growth rates, depicted in Figure 3b, decreases with increasing temperature showing that the formation of volatile suboxides is favorable at higher growth temperatures. For the highest investigated oxygen pressure of 0.006 mbar saturation of the growth rate with values between 24.5 to 26.2 pm/pulse is observed for growth temperatures below 550 °C.

![Figure 3](image-url) **Figure 3.** (a) Cation concentration of gallium, aluminum and silicon atoms measured by EDX in dependence of the growth pressure deposited at a growth temperature of 670 °C. The dotted lines indicate elemental concentration for a stoichiometric transfer of the target composition being \(x_{Ga} = 0.868, x_{Al}^{\text{stoch}} = 0.088\) and \(x_{Si}^{\text{stoch}} = 0.044\). (b) Dependency of the growth rate on the growth temperature for three chosen oxygen pressures as labeled in the picture.

Using AFM on areas of \(3 \times 5 \mu \text{m}^2\) the surface morphology and consequently the mean square roughness \(R_q\) and peak-valley-distance \(d_{PV}\) are observed and results in similar growth rates and bandgaps (see Fig. 2). In the oxygen regime below 0.016 mbar, aluminum atoms are preferentially incorporated, because of the higher dissociation energy of the Al-O bond compared to the Ga-O bond.\(^{15}\) Further, gallium forms volatile sub-oxides being desorbed. As a result, considerably lower amounts of Ga are incorporated into the layers as seen in Figure 3a. The higher aluminum content leads to the observed bandgap increase and the desorption of gallium sub-oxides leads to lower growth rates. Similar desorption processes were reported for molecular beam epitaxial growth of In\(_2\)O\(_3\), Ga\(_2\)O\(_3\) and (In\(_{x}\)Ga\(_{1-x}\))\(_2\)O\(_3\) thin films by Vogt and Bierwagen.\(^{26–28}\) Since the desorption is a temperature dependent process, we investigated the growth rates of samples deposited at three different oxygen pressures (0.006, 0.001 and \(3 \times 10^{-4} \text{ mbar}\)) and various growth temperatures (from 400 to 670 °C). For deposition of these sample series we used a target consisting of Ga\(_2\)O\(_3\) + 8.8 at.% Al\(_2\)O\(_3\) + 0.6 at.% SnO\(_2\). The growth rates, depicted in Figure 3b, decreases with increasing temperature showing that the formation of volatile suboxides is favorable at higher growth temperatures. For the highest investigated oxygen pressure of 0.006 mbar saturation of the growth rate with values between 24.5 to 26.2 pm/pulse is observed for growth temperatures below 550 °C.

![Figure 4](image-url) **Figure 4.** \(R_q\) describes the mean square roughness and \(x\) the aluminum content. The scale next to the pictures (a) to (d) characterizes the peak-valley-distance \(d_{PV}\). The thin films are deposited at \(T_g = 670 \degree C\) and different oxygen partial pressures as labeled. (e) shows the dependency of \(R_q\) and \(d_{PV}\) to the oxygen pressure.
This issue must be solved prior to the fabrication of devices based on (Al,Ga)2O3. We described that the preferential incorporation of Al was inhomogeneous dopant concentration of approximately (1–5) × 10^{18} cm^{-3} was realized for both, Si and Sn, as visible in Fig. 5. Before and after annealing, however, all samples remained insulating as soon as Al was alloyed.

### Conclusions

We have discussed the influence of growth conditions on the crystallinity, bandgap energy, growth rate, cation composition and surface morphology of PLD-grown (Al,Ga)2O3 thin films on c-sapphire substrates. We described that the preferential incorporation of Al was in tendency observed for low oxygen pressures and/or high growth temperature, which was assigned to differences in cation oxygen bond strength and desorption of gallium sub oxide. Decreasing growth pressure lead to decreasing growth rates and low gallium content. Lower growth temperatures favor the stoichiometric cation incorporation into the thin film layer. Further, many different growth conditions were pointed out to produce insulating samples. It can be concluded that it was not possible to produce conductive samples. This issue must be solved prior to the fabrication of devices based on (Al,Ga)2O3.

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