Highly Conductive Co-Doped Ga$_2$O$_3$:Si-In Grown by MOCVD

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Abstract: We report a highly conductive gallium oxide doped with both silicon and indium grown on c-plane sapphire substrate by MOCVD. From a superlattice structure of indium oxide and gallium oxide doped with silicon, we obtained a highly conductive material with an electron hall mobility up to 150 cm$^2$/V·s with the carrier concentration near 2 × 10$^{17}$ cm$^{-3}$. However, if not doped with silicon, both Ga$_2$O$_3$:In and Ga$_2$O$_3$ are highly resistive. Optical and structural characterization techniques such as X-ray, transmission electron microscope, and photoluminescence, reveal no significant incorporation of indium into the superlattice materials, which suggests the indium plays a role of a surfactant passivating electron trapping defect levels.

Keywords: MOCVD; metal oxide; high electrical performance; doping with silicon; Ga$_2$O$_3$ poly-morph

1. Introduction

Gallium oxide (Ga$_2$O$_3$) has drawn much attention due to its potential for realizing next generation ultra-wide band gap (UWBG) electronic/optoelectronic device applications such as high-power transistors or ultraviolet (UV) solar blind photodetectors (SBPD). Of five possible different polymorphic forms (α-, β-, γ-, δ-, and κ) [1,2], single crystal β-Ga$_2$O$_3$ exhibits a relatively high breakdown voltage compared with those of other wide bandgap materials, such as GaN or SiC. In addition, alloying with other elements such as indium, aluminum or magnesium allows for band gap engineering within the ultraviolet C light (UVC) solar blind band (200–280 nm) [3–5]. These potential advantages, along with the presence of commercially available single crystal substrates, have drawn considerable interest in utilizing β-Ga$_2$O$_3$ in many important technological applications from transparent electrodes, thin film transistors and gas sensors to solar blind photodetectors and light-emitting diodes (LED) emitting in UVC band [6]. Besides the commonly investigated β-Ga$_2$O$_3$, there has been a growing interest in the metastable phase of Ga$_2$O$_3$, such as κ or c-phase, as those phases also exhibit a wide band gap energy near 4.8 eV, in addition to the fact that they are often readily obtained by heteroepitaxy when grown on hexagonal substrates such as MgO or Al$_2$O$_3$ [7–13]. Furthermore, κ-Ga$_2$O$_3$ is predicted to possess a large spontaneous polarization value (~26 μC/cm$^2$) along c-direction, which have attracted a significant interest in scientific community [14]. In a recent report [15], we also have shown that κ-Ga$_2$O$_3$ can be grown on c-plane sapphire substrates. In addition, we have reported that the phase of as-grown κ-Ga$_2$O$_3$ on c-plane sapphire substrates can be changed to β-phase upon annealing at 1000 °C [16]. This as-grown κ-Ga$_2$O$_3$ was highly resistive to be applied for practical electronic applications. In order to realize high-performance electronics, controlling conductivity of epitaxial layers is an important factor. For instance, both a highly resistive buffer layer and a subsequently grown conductive layer are the structure commonly employed for electronic devices with high performance [17,18]. Although a conductive metastable ε-Ga$_2$O$_3$ grown by metal organic chemical vapor deposition (MOCVD) was presented, the reported hall mobility at room temperature was in...
the range of 1–5 cm²/V·s with the electron concentration near 3 × 10¹⁸ cm⁻³ [19]. These mobility values are not as high as those reported from β-Ga₂O₃ [20,21], which resulted in a relatively high device performance. In this present work, we demonstrate a highly conductive co-doped Ga₂O₃:Si-In with a high electron mobility up to ~150 cm²/V·s at room temperature grown by MOCVD on c-plane sapphire substrate, with carrier concentration of 2 × 10¹⁷ cm⁻³.

2. Materials and Methods

We grew different superlattice structures consisting of oxide layers with various doping at 690 °C under H₂ carrier gas using Trimethyl-gallium (TMGa) and Trimethyl-indium (TMIn), pure H₂O vapor and Silane (SiH₄) as Ga, In, O and Si precursors, respectively, grown by Aixtron horizontal AIX200/4 MOCVD reactor. The growth details for the materials as well as conditions of post ex situ and in situ annealing can be found in our previous report [16]. Detail information about different superlattice structures is summarized in Table 1.

| Structure   | Type of Superlattice                  | Ga   | In   | H₂O  | Si  |
|-------------|---------------------------------------|------|------|------|-----|
| Structure 1 | Ga₂O₃ (Reference)                     | 5 sccm| 0 sccm| 1600 sccm | 20 sccm |
| Structure 2 | Ga₂O₃ (30 s)/In₂O₃ (1 min)            | 5 sccm| 50 sccm| 1600 sccm | 20 sccm |
| Structure 3 | Ga₂O₃ (30 s)/In₂O₃ (1 min)            | 5 sccm| 70 sccm| 1600 sccm | 20 sccm |
| Structure 4 | Ga₂O₃ (1 min)/(InₓGa₁₋ₓ)₂O₃ (1 min)   | 5 sccm| 70 sccm| 1600 sccm | 20 sccm |

3. Results and Discussion

We performed several characterizations for the samples listed in Table 1. At first, through scanning electron microscope (SEM), we measured the total thickness of the superlattice structures shown in Figure 1. All of the deposited superlattice layers have an equivalent growth rate regardless of the TMIn flow rate during the growth. For example, the reference Ga₂O₃:Si (Structure 1) was deposited with a rate of 16.8 nm/min while that of Ga₂O₃:Si/(InₓGa₁₋ₓ)₂O₃:Si (Structure 4) was 17.2 nm/min showing the error range of 0.2 nm/min. This possibly indicates that In₂O₃ was not formed or the growth of In₂O₃ was formed in non-layer-by-layer fashion.

![Figure 1](image_url)

**Figure 1.** (a) The summary of growth rate depending on the Trimethyl-indium (TMIn) flow rate. (b) The cross-sectional SEMs image of Ga₂O₃ reference growth.
The X-ray diffraction (XRD) patterns shown in Figure 2 also support the fact that indium would not be properly formed as a layer. All the as-grown samples exhibit the same peak positions corresponding to \( \kappa\)-Ga\(_2\)O\(_3\) (002), (004), and (006) reflections. Particularly, neither superlattice satellite peaks nor peak position shift were observed from the superlattice structures in spite of the fact that TMIn was supplied during the growth. This result indicates that the incorporated indium is small enough not to cause a change in the out of plane lattice parameter. These samples also showed the evidence of phase transition from \( \kappa\)- to \( \beta\)-phase upon annealing at 1000 °C, which is in agreement with our previous study [16]. Although phase transition occurred after the annealing process, no evidence of the peak shifts in either (310) or (620) peaks were observed. If In\(_2\)O\(_3\) was grown and subsequent indium diffusion happened after the annealing at 1000 °C, one would expect to observe peak shift in (310) and (620) peaks as the diffused indium atoms will replace Ga atoms and the lattice parameter should subsequently change, which was not observed in our study. This observation suggests that the incorporated indium is in a small degree since substantial indium incorporation should result in a higher growth rate as a result of increased group III molar flow rate or cause to make peak shifts in XRD data.

![Figure 2. XRD patterns from the various (a) as-grown superlattice structures and (b) the annealed samples listed in Table 1.](image)

In order to further investigate the indium incorporation in the superlattice structures, energy-dispersive X-ray spectroscopy (EDS) taken along with scanning transmission electron microscopic ((S)TEM)) analysis was carried out for the superlattice sample grown with 70 sccm (standard cubic centimeters per minute) of TMIn flow rate (Structure 3). As shown in Figure 3, no evidence of indium containing nanostructure was observed below its detection limit (0.1 wt.%), which is in line with the identical multiple peaks in the XRD patterns as well as the nearly constant growth rate. Therefore, based on the aforementioned characterization data, we confirmed that no significant amount of indium incorporation has been found in all of the superlattice structure.
Although the indium was not incorporated within the superlattice structures, we found remarkable improvement in electrical characteristics of samples. Table 2 summarizes the electrical performance measured from all different types of films (From Structure 1 to Structure 4). In contrast to the electrically resistive as-grown $\kappa$-Ga$_2$O$_3$:Si ($\rho > 2000 \ \Omega \cdot \text{cm}$) noted as Structure 1, all of the as-grown superlattice structures (Structure 2,3,4) exhibited a high conductivity with the resistivity as low as $\rho = 0.69 \ \Omega \cdot \text{cm}$. For instance, the hall mobility of $150 \ \text{cm}^2/\text{V} \cdot \text{s}$ was obtained from the In$_2$O$_3$:Si based superlattice structure grown with 70 sccm of TMIn flow rate (Structure 3), which is higher by several times than the any other values measured from other structures. These as-grown In$_2$O$_3$ based superlattice samples (Structure 2 and Structure 3) exhibited generally higher electron mobilities by a factor of 3~15, in comparison to the values obtained from the Ga$_2$O$_3$:Si/(In$_x$Ga$_{1-x}$)$_2$O$_3$:Si based superlattice layer (Structure 4), with the electron concentration ranging from $2 \times 10^{17}$ to $1.3 \times 10^{18} \ \text{cm}^{-3}$. This phenomenon can be explained by the previous experiments that indium has been known as an effective surfactant to improve dislocation densities, surface roughness, carrier mobilities and activated carrier densities within GaN-based system [22–27]. In the past, we reported that by adding TMIn during AlGaN growth, remarkable improvement in hall mobility has been observed since TMIn helps to relieve strains, making crack-free growth of AlGaN on sapphire substrate [22,23]. Although our superlattice structures are formed without having cracks on surface, TMIn showed similar effects in oxide growth as well, leading to the improved conductivity. On the other hand, it must be noted that all of the superlattice structures grown without silane as a dopant resulted in a high resistivity before (>11800 $\Omega \cdot \text{cm}$) and even after annealing (>9050 $\Omega \cdot \text{cm}$). This result has alluded to the fact that the silicon plays a role as a shallow donor, while indium acts as a surfactant which helps enhance the activation of silicon within the metastable $\kappa$-Ga$_2$O$_3$. 

![Figure 3. Energy-dispersive X-ray spectroscopy (EDS) analysis performed from the as-grown superlattice structure based on In$_2$O$_3$ grown with 70 sccm of TMIn (Structure 3) through both TEM and SEM.](image-url)
Table 2. Summary of the Hall measurement data performed from all of the superlattice layers listed in Table 1.

| Structure   | Before Annealing Process | After Annealing Process |
|-------------|--------------------------|-------------------------|
|             | Hall Mobility            | Carrier Concentration   | Hall Mobility | Carrier Concentration |
| Structure 1 | Not measurable           | Not measurable          | 14 cm²/V·s   | 2 × 10¹⁸ cm⁻³         |
| Structure 2 | 30 cm²/V·s              | 1.3 × 10¹⁸ cm⁻³         | 27.6 cm²/V·s | 1.35 × 10¹⁹ cm⁻³      |
| Structure 3 | 150 cm²/V·s             | 2 × 10¹⁷ cm⁻³           | 13.8 cm²/V·s | 2 × 10¹⁹ cm⁻³         |
| Structure 4 | 10 cm²/V·s              | 9.26 × 10¹⁷ cm⁻³        | 29 cm²/V·s   | 3 × 10¹⁸ cm⁻³         |

Normalized photoluminescence (PL) spectra were taken from all of the as-grown (Figure 4a) and annealed (Figure 4b) superlattice samples listed in Table 1. After annealing process and the subsequent phase transition to β phase, the peak position has shifted near 360 nm which is similar to β-phase Ga₂O₃ substrate while the peak around 420 nm seems to be related to κ phase, in accordance with our previous results [16]. Apart from the change in the PL peak, other noticeable traits depending on the amount of TMIn during the growth have not been observed, supporting the fact that indium acts as a surfactant rather than being deposited. Although we found the PL peak might be related to the phase of materials, discovering the origin of PL emission peaks is our ongoing research and thus further investigation is required to provide a clear interpretation of PL data.

Figure 4. Photograph luminescence spectra from all of the (a) as-grown and (b) annealed superlattice structures. Transmission measurement of (c) as-grown and (d) annealed superlattice layers for obtaining the optical bandgap.

Transmission measurement had also been conducted in order to calculate the optical bandgap of the samples. We discovered the evidence of a decrease in bandgap energy as a result of the phase transition caused by the annealing process at 1000 °C. The (αE)² plots demonstrated that the phase variation from κ- to β-phase leads to a decrease in optical energy bandgap for the superlattice structures. Specifically, through a linear fitting,
an extracted direct bandgap energy of 4.72 eV for the as-grown samples was measured whereas the optical bandgap energy of the annealed superlattice structures was reduced to 4.66 eV, indicating that the phase transition may have an influence on the direct bandgap energy. However, similar to the previous observation in PL, regardless of the supply of TMIn during the growth, none of the superlattice samples had represented different optical characteristics compared to the reference. Therefore, based on the PL and transmission measurement data, it suggests that the energy gap of β-phase layers is lower than the one of κ-phase Ga₂O₃-based material systems.

4. Conclusions
Highly conductive co-doped Ga₂O₃:Si-In films grown on c-plane sapphire substrate were demonstrated with a significantly high electron mobility. Structural characterization represented that under H₂ condition as a carrier gas, the samples were grown having metastable κ-phase whereas the annealed samples became β-phase in either case of whether we doped with silicon or not. When the materials were not doped with silicon, both as-grown and annealed thin films had a high resistivity. Also, even if silicon was added as a dopant during the growth, the as-grown layers still had a high resistivity. On the other hand, when doped with silicon and supply the TMIn during the growth, a significantly improved electron hall mobility up to 150 cm²/V·s had been observed in as-grown samples, showing a tendency that a higher flow of TMIn led to an increase in the mobility. Other characterizations such as cross-sectional SEM, and EDX analysis indicate that no significant fractional indium incorporation takes place. Rather, the TMIn flow during the various superlattice growths leads to indium at the growth front acting as a surfactant enhancing the electron hall mobilities. This observation indicates the silicon is a shallow donor within co-doped Ga₂O₃:Si-In while indium acts a surfactant which enhances the hall mobility. The findings presented in this report are crucial in realizing high-performance electronic applications such as high-power transistors where the control of electrical conductivity is important.

Author Contributions: Data curation, J.L.; formal analysis, J.L. and L.G.; investigation, J.L.; project administration, M.R.; software, H.K.; validation, J.L.; writing—original draft, J.L. and H.K.; writing—review and editing, J.L. and M.R. All authors have read and agreed to the published version of the manuscript.

Funding: This work is supported by Air Force under agreement of FA9550-19-1-0410.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data presented in this study are available on request from the corresponding author.

Acknowledgments: This work is supported by Air Force under agreement of FA9550-19-1-0410. The authors would like to acknowledge the support and interest of Ali Sayir of USAF-AFMC AFMCAFOSR/RTB). The (S)TEM characterizations made use of the EPIC facility of Northwestern University’s NUANCE Center, which has received support from the SHyNE Resource (NSF ECCS-2025633), the IIN, and Northwestern’s MRSEC program (NSF DMR-1720139). The authors would like to acknowledge Vinayak P. Dravid, Xiaobing Hu and Kun He as well.

Conflicts of Interest: The authors declare no conflict of interest.

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