Direct observation of site-specific dopant substitution in Si doped (Al\textsubscript{x}Ga\textsubscript{1−x})\textsubscript{2}O\textsubscript{3} via atom probe tomography

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Abstract

In this work, the interaction of n-type dopants in Si doped (Al\textsubscript{x}Ga\textsubscript{1−x})\textsubscript{2}O\textsubscript{3} films with varying Al content over the entire composition range (x = 0\%−100\%) was analyzed using atom probe tomography. An almost uniform dopant distribution with dopant density in the range of 10\textsuperscript{18} cm\textsuperscript{−3} was obtained in (Al\textsubscript{x}Ga\textsubscript{1−x})\textsubscript{2}O\textsubscript{3} layers with Al contents, x < 0.60. At x ≥ 0.6, small Si segregated zones were observed which was attributed to the increased donor-acceptor transition centers or bond length differences in Al–O, Ga–O and Si–O at high Al content. We have demonstrated that for the single phase β-(Al\textsubscript{x}Ga\textsubscript{1−x})\textsubscript{2}O\textsubscript{3} films with Al content of x < 0.30, dopants prefer to occupy on Ga sites while Al site is preferred for high Al content (x > 0.50) (Al\textsubscript{x}Ga\textsubscript{1−x})\textsubscript{2}O\textsubscript{3} layers. It was also observed for Al content, x = 0.30−0.50, no specific cationic site occupancy was observed, Si occupies either Al or Ga sites. This can be attributed to highly inhomogeneous layers within this Al composition range due to which dopant Si atoms are either in the Al-rich or Al-depleted regions.

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Keywords: Si doped (Al\textsubscript{x}Ga\textsubscript{1−x})\textsubscript{2}O\textsubscript{3}, n-type dopant, site occupancy, atom probe tomography

(Some figures may appear in color only in the online journal)

1. Introduction

(Al\textsubscript{x}Ga\textsubscript{1−x})\textsubscript{2}O\textsubscript{3} is a thermodynamically stable ultra-wide bandgap semiconductor with a high predicted breakdown field and higher Baliga’s figure of merit, making it a rising candidate for future high power switching devices and deep ultra-violet (DUV) optical applications [1–3]. (Al\textsubscript{x}Ga\textsubscript{1−x})\textsubscript{2}O\textsubscript{3} has already demonstrated its potential in high speed field effect transistors [4], Schottky barrier diodes [5] and DUV photodetectors [6]. For these devices to perform up to their theoretical limit, extrinsic n-type doping is necessary since intrinsic defects i.e. oxygen vacancies do not significantly contribute in conduction [7, 8]. Si, Sn, and Ge are being considered as suitable dopants for (Al\textsubscript{x}Ga\textsubscript{1−x})\textsubscript{2}O\textsubscript{3} inspired by the high dopant density as well
as controlled doping profile achieved in the case of Ga$_2$O$_3$ based devices \cite{8-10}. Although, Si doping in (Al, Ga)$_{1-x}$O$_3$ has been reported by Bhuiyan \textit{et al} \cite{11}, Ranga \textit{et al} \cite{12}, and Hassa \textit{et al} \cite{8} recently, doping of (Al, Ga)$_{1-x}$O$_3$ films is still in its infancy and needs adequate understanding.

Impurity doping is often associated with the formation of specific native defects and these defects are more likely to diffuse towards the active bulk region \cite{13}. In Ga$_2$O$_3$, it was observed that Si substitutes on the Ga site and contributes to shallow or deep level defect states as well as structurally complex defects \cite{13, 14}. Similar Si occupancy on the Ga site (Si$_{Ga}$) was reported for GaAs and GaN with the formation of a complex defect with Ga vacancies, V$_{Ga}$, (V$_{Ga}$–Si$_{Ga}$) \cite{15, 16}. In AlGaN, although Si can occupy either Ga or Al site \cite{16}, at higher Al content of >60\%, V$_{III}$$–$Si$_{III}$ defect complexes on Al site (V$_{Al}$–Si$_{Al}$) are more common owing to the increasing amount of V$_{Al}$ formation \cite{13, 17}. These defects induced by Si doping are electrically active \cite{18} and can directly affect the electrical and optical performance of the fabricated devices by acting as charge trapping centers. Electron concentration, hence carrier mobility is observed at high doping level (up to \(10^{17}\) cm$^{-3}$), while at higher doping level (\(>\) mid-\(10^{18}\) cm$^{-3}$), a decrease in free electron concentration (and carrier mobility) is observed due to a variety of compensating defects formation resulting from cationic (Ga or Al site) substitution \cite{19}. This phenomenon is termed as the compensation knee. The mechanism and specification of the predominant defects (V$_{Ga}$–Si$_{Ga}$ or V$_{Al}$–Si$_{Al}$) responsible for this compensation knee, i.e. reduced carrier mobility with high doping level have not been conclusively understood yet for (Al, Ga)$_{1-x}$O$_3$. Therefore, it is critical to have a clear understanding of how the n-type Si doping interacts with (Al, Ga)$_{1-x}$O$_3$ matrix to realize high mobility devices.

To gain a deep insight into dopant interaction in (Al, Ga)$_{1-x}$O$_3$ films, atomic level investigation of doping chemistry is desired. Atom probe tomography (APT) is an advanced nanoscale characterization tool enabling 3D visualization of constituent elements atom by atom with excellent spatial and chemical resolution \cite{20}. APT is capable of providing information of each dopant’s locations and atomic distribution in the neighboring sites in the host materials \cite{21}. This can be used to frame specific site occupancy by individual dopant atoms and would be crucial to account for the compensation effect resulting from cation specific defect complex like V$_{III}$–Si$_{III}$. In this paper, we employed APT to study dopant’s interaction in Si doped (Al, Ga)$_{1-x}$O$_3$ films with varying Al content over the whole composition range of \(x = 0\)–1.0. A statistical analysis method, radial distribution function (RDF), was adapted to elucidate the mechanism of dopant’s incorporation in (Al, Ga)$_{1-x}$O$_3$ films. Since high Al content in (Al, Ga)$_{1-x}$O$_3$ is required for bandgap enlargement, a critical understanding of subsequent dopant’s interaction in these films at different Al contents will be significant for the realization of high performance (Al, Ga)$_{1-x}$O$_3$ based devices.

2. Experimental section

The Si doped (Al, Ga)$_{1-x}$O$_3$ heterostructure with varying Al content, \(x = 0, 0.10, 0.20, 0.30, 0.40, 0.50, 0.60, 0.80\) and 1.0 with a thickness of 20 nm each were grown by metal organic chemical vapor deposition on Fe-doped semi-insulating (010) $\beta$-Ga$_2$O$_3$ substrates (from Novel Crystal Technology, Inc.). Details of the growth can be found elsewhere \cite{11, 22}. The details about the tested sample and sample quality is described in \cite{22}. For APT specimen preparation, an additional (Al$_{0.30}$Ga$_{0.70}$)$_2$O$_3$ layer (50 nm) was deposited as a sacrificial layer on top of the (Al, Ga)$_{1-x}$O$_3$ heterostructures. The focused ion beam milling method was used to prepare needle-shaped specimens following standard lift-out and annular milling procedure as reported by Thompson \textit{et al} \cite{23}. APT experiment was performed using pulsed laser assisted CAMECA Local Electrode Atom Probe (LEAP 5000X HR) system at a specimen base temperature of 50 K under ultra-high vacuum of \(<10^{-11}\) mbar. The controlled field evaporation of atoms from the needle-shaped specimen was achieved by employing a UV laser at a pulse energy of 20 pJ. The pulse frequency was 200 kHz and the detection rate was 0.005 atoms per pulse. CAMECA’s Integrated Visualization and Analysis Software (IVAS, version 3.6.14) was used for 3D reconstruction of the specimen and advanced data analysis. Statistical analysis was conducted by RDF over small bulk volumes (15 \(\times\) 15 \(\times\) 8 nm$^3$) in each (Al, Ga)$_{1-x}$O$_3$ layers to investigate the nearest neighbor distribution of elements to understand the dopant incorporation mechanism in these films.

3. Results

Figure 1(a) illustrates the schematic diagram of the (Al, Ga)$_{1-x}$O$_3$ heterostructures with different Al content of \(x = 0\%–100\%\) layers along the growth direction. Details about this structure is reported in \cite{22, 24}. The mass spectrum corresponding to a volume of 25 \(\times\) 25 \(\times\) 200 nm$^3$ extracted from the bulk region of the tip for the (Al, Ga)$_{1-x}$O$_3$ layers up to first 10 nm of the Al$_2$O$_3$ layer is shown in figures 1(b)–(d). The dopant Si was identified by the Si$^{+1}$ peak at 28 Da and Si$^{+2}$ peak at 14 Da in the background corrected mass spectrum. Such Si peaks were not observed in the mass spectrum of undoped (Al, Ga)$_{1-x}$O$_3$ as shown in supplementary figure S1 (available online at stacks.iop.org/JPD/54/184001/mmedia). Potential Al$^{+1}$ peak at 28 Da was absent as confirmed by comparing the mass spectrum of undoped and Si doped (Al, Ga)$_{1-x}$O$_3$ (figures S1 and S2) and \cite{25}, thereby enabling confident labeling of Si peaks in this case. We observed Al thermal tails in the mass spectrum, especially for higher Al content layers that might influence the Si count from their designated mass peaks, and was carefully assessed (see figures S1 and S2 and table S1 in the supplementary document). Potential peak overlapping for Si peaks at 28 Da and 14 Da with the thermal tails from the neighboring Al$^{+1}$ peak at 27 Da and Al$^{+2}$ peak at 13.5 Da was not significant, as illustrated
by the magnified view of the mass spectrum around the Si\(^{2+}\) peak at 14 Da (in figure 1(c)) and around the Si\(^{2+}\) peak at 28 Da (in figure 1(d)). The contribution of Al thermal tails into the Si peaks in the overall data analysis is discussed at the end of the result section and in the supplementary document. Figure 2(a) depicts the APT reconstructed 3D volume of the graded (Al\(_x\)Ga\(_{1-x}\))\(_2\)O\(_3\) heterostructure highlighting Al distribution along with the layers with \(x = 0\%–100\%\). In this representation, a temperature color map was used to observe the Al concentration variation along the heterostructure with red representing the highest Al concentration (\(x = 1.0\)) while the lowest Al concentration (\(x = 0\)) is shown in blue. This color temperature variation enables to identify each layer with different Al contents. From the temperature color map, it is observed that, at Al content, \(x < 0.30\) and \(x > 0.50\), a low color contrast is observed indicating homogeneity of these layers. A small amount of Al accumulation is observed in the layer with \(x = 0.10\) which is negligible. When Al content, \(x \geq 0.30\) and \(x \leq 0.60\), a higher contrast in color maps with relatively higher Al at the center compared to at the edge regions is observed indicating inhomogeneous Al distribution in these layers.

The detailed analysis of alloy composition variation for this similar structure is reported in our earlier work [22, 24]. To visualize the dopant incorporation within this heterostructures, lateral Si distribution in XY planes, perpendicular to the growth direction was plotted for 4 nm thick volumes (~31 atoms nm\(^{-3}\)) extracted from the bulk regions of each layer as depicted in figures 2(b)–(j). For statistical comparison of dopant distribution from each layer, the number of atoms/volume was kept constant by varying the individual volume that varies with the tip shape and geometry along the growth direction. From the initial visualization of lateral Si distribution in each (Al\(_x\)Ga\(_{1-x}\))\(_2\)O\(_3\) layer in figures 2(b)–(g), it is confirmed that a closely random dopant distribution is obtained with a dopant concentration of \(\sim 1–7 \times 10^{18} \text{ cm}^{-3}\). The measured dopant concentration closely resembles with the concentration range expected from the average dopant incorporation of \(\sim 1–5 \times 10^{18} \text{ cm}^{-3}\) during the epi-growth. This implies, desired dopant incorporation with a closely uniform dopant profile is achieved for the layers with Al content, \(x \leq 0.5\). However, in the lateral Si distribution plots, several small island-like high Si concentration regions are observed when Al content, \(x \geq 0.60\) as shown in figures 2(h)–(j). Such small non-uniformity in the dopant distribution may arise from increased donor-acceptor (DX) transitions [26] or the bond length difference of Al–O to that of Ga–O and Si–O at high Al content [27].

Also, the Si count being very low in this case, the vertical projection of two or more Si atoms in the same or closely located XY planes (two Si ions overlaid on each other as shown in the supplementary figures S3 and S4) would contribute in high density regions in lateral Si distribution. Therefore, additional statistical analysis is necessary to determine the uniformity of dopant distribution.

Each (Al\(_x\)Ga\(_{1-x}\))\(_2\)O\(_3\) layer was investigated individually to verify the Si distribution and whether the dopants are forming any cluster or not. A statistical method, frequency distribution analysis (FDA) of Si distribution was conducted from the similar bulk volumes from each layer those were used for lateral
Si distribution in figures 2(b)–(j) using a 300 atoms bin size. In FDA, any deviation of observed elemental distribution from a binomial fitting represents the presence of elemental segregation or inhomogeneity in the layer [28]. The FDA results for Si in (Al<sub>x</sub>Ga<sub>1−x</sub>)<sub>2</sub>O<sub>3</sub> films with x = 0%–100% are shown in figures 3(a)–(i). It is observed that, for each case, the observed Si distribution closely resembles the binomial fit for random (uniform) elemental distribution. The Pearson coefficient, µ tending towards 1 suggests statistically significant elemental segregations [28]. The very low µ-values (⩽0.05) in the layers with x < 0.60 suggest that no statistically considerable Si segregation is present in these layers.

The null hypothesis testing of Si distribution provides a low P-value (0.05–0.1) for the (Al<sub>x</sub>Ga<sub>1−x</sub>)<sub>2</sub>O<sub>3</sub> layers with x < 0.6 which suggests, the null hypothesis can be rejected at a 90%–95% confidence level and Si has a distribution which is statistically similar to a binomial random distribution. In the layers with higher Al content, x ⩾ 0.6, although the observed Si distribution is not significantly deviating from the binomial fitting, the µ-values are relatively higher (approximately ~0.1). This relatively higher µ-values are indicating that, small Si-rich regions (non-uniformity) are present in these layers with an 80%–85% confidence level. It is to be noted that, although the µ-values in the (Al<sub>x</sub>Ga<sub>1−x</sub>)<sub>2</sub>O<sub>3</sub> layers with x ⩾ 0.6 is relatively higher suggesting small Si-rich regions, the observed Si distribution resembling with the binomial fitting. Such discrepancy could be due to low Si counts within these layers and further investigation is needed for a conclusive statement.

As the alloy composition is changing substantially, it is crucial to understand the mechanism at which dopants are interacting with the matrix. A statistical analysis method, RDF was applied to the APT data to understand the dopant chemistry within the alloy matrix. RDF determines the radial concentration profile starting from each atom detected for specifically chosen species and returns the probability density of finding an atom j at a distance r given that an atom i being the center [29]. RDF normalizes the local concentration of a selected species to the bulk concentration within the volume selected. The RDF function works in a radially outward direction from each center atom of interest and the measured bulk concentration is averaged across the sample [30]. To explain the neighboring chemistry of dopant Si atoms, a series of 15 nm × 15 nm × 8 nm volumes were extracted from the bulk regions of each (Al<sub>x</sub>Ga<sub>1−x</sub>)<sub>2</sub>O<sub>3</sub> (x = 0%–100%) layers to perform RDF. Figure 4(a) illustrates the operation of RDF in this study where each Si is considered as a center atom and starting from that origin, the bulk normalized concentration (BNC) of other detected species (Al, Ga, and O) were measured. Figures 4(b) and (c) illustrates the RDF analysis of
Figure 3. (a)–(i) Frequency distribution analysis for Si distribution in (Al$_{x}$Ga$_{1-x}$)$_2$O$_3$ layers with $x = 0\%$–100\%, showing statistically uniform Si distribution in all layers with $x < 0.6$.

Figure 4. (a) A schematic diagram illustrating the operation of radial distribution function; RDF result on dopant Si atom in (b) Ga$_2$O$_3$ showing Si is occupying in Ga site, (c) Al$_2$O$_3$ showing Si is occupying in Al site. In both case, O concentration surrounding the center Si atoms position is zero indicating cationic substitution by the dopants. Ga$_2$O$_3$ ($x = 0\%$) and Al$_2$O$_3$ ($x = 100\%$), showing BNC for Ga and Al, respectively with BNC of O as reference considering Si atoms at the origin (distance, $d = 0$). An average randomized comparator of multiple random data sets is provided in both case to realize the significance of the BNC for Ga, Al and O. The random comparators represent the expected distribution of the solute atoms considering there is no correlations in the spatial distribution of these atoms [31]. The deviation of RDF results from such random comparators indicates the tendency of clustering or anti-clustering in the distribution
of any species of interest [31]. In any particular position, if the elemental distribution is significantly higher than the randomized comparator, it implies the presence of clustering or segregation of that element while the concentration profile being considerably lower than the random comparator would imply an anti-clustering/depletion in the elemental distribution which could be due to the presence of vacancies. The BNC for O remains zero up to radially outward few nearest neighbor locations over a distance of 0.2–0.3 nm in both cases as illustrated in figures 4(b) and (c). In both cases, BNC for cationic species, either Ga or Al in Ga₂O₃ or Al₂O₃, respectively, is higher in the radially outward positions (d > 0) surrounding the dopants located at the center (d = 0). The high Ga or Al concentrations surrounding the Si atoms indicates, dopant Si atoms are more likely occupying in Ga site in Ga₂O₃ as in figure 4(b) or Al site in Al₂O₃ as in figure 4(c).

Information on such specific site occupancy was obtained by APT previously in voltage pulsing mode for metallic alloys using spatial distribution maps and atom vicinity analysis [31, 32]. Such analysis was not feasible in this case because the analyzed structure is a non-metallic system and laser pulsing was used to evaporate the ions. Hence, crystallographic poles were not observed in the detector map due to non-sequential evaporation resulting from the thermal migration of ions [33]. Therefore, lattice planes were not visible in the 3D tip reconstruction. However, the site occupancy information was interpreted from the neighboring chemistry revealed by RDF. In Ga₂O₃ and Al₂O₃, the average spacing between a cationic (Ga or Al) site and the neighboring O site is ~0.2 nm [34, 35] which is comparable to what was observed by RDF plots in figures 4(b) and (c). The small deviations of site spacing between Ga (or Al) and O sites can be attributed to the thermal migration of ions due to laser pulsing that adversely affects the desired sequential evaporation [36]. These may lead to artifacts in the measured site spacing via RDF by reducing the spatial resolution along the lateral XY plane while providing higher resolution in z-planes [36, 37]. At the reference dopant atoms’ position (d = 0), BNC for Ga and Al drops to zero as shown in figures 4(b) and (c), respectively. This implies the presence of cation vacancies (VₓGa in Ga₂O₃ and VₓAl in Al₂O₃) and dopants are interacting with these cationic vacancies [13, 16]. Such specific cationic site occupancy of Si and its interaction with cation vacancies would lead to the formation of complex defects such as VₓGa–SiₓGa or VₓAl–SiₓAl as observed in the case of GaN or GaAs and AlN [13, 15–17]. Considering the RDF results showing cationic substitution for x = 0 (Ga₂O₃) and x = 1.0 (Al₂O₃) as a reference, we investigated cation (Ga or Al) site substitution by dopant in rest of the alloy composition with 0 < x < 100 in the next part of this paper.

Since the alloy composition is varying with Al content from x = 0% to 100%, we extended our analysis to other (AlₓGa₁₋ₓ)₂O₃ layers with x > 0 and x < 1.0. In these layers, there are both Ga and Al sites that Si dopants can occupy. The RDF analysis for (AlₓGa₁₋ₓ)₂O₃ films with x = 10%, 20%, 30%, 40%, 50%, 60% and 80% are illustrated in figures 5(a)–(i). At low Al content, x = 10%–20%, RDF

Figure 5. Radial distribution function results in each (AlₓGa₁₋ₓ)₂O₃ layers showing Si is occupying (a)–(c) Ga site at (AlₓGa₁₋ₓ)₂O₃ at x = 0.10–0.20; (d)–(f) Ga or Al site at (AlₓGa₁₋ₓ)₂O₃ at x = 0.30–0.50; (g)–(i) Al site at (AlₓGa₁₋ₓ)₂O₃ at x = 0.60–0.80.
analysis shows that in the proximity of the center Si atoms up to few nearest neighbor locations, BNC for Ga is higher while that for Al is low (BNC ∼ 0 for Al) as depicted in figures 5(a)–(c). This could be an indication of Si atoms are likely to occupy on Ga site. At the center Si atoms (d = 0), BNC for Ga drops significantly, implying the presence of V_{Ga} (figures 5(a)–(c)). This suggests that the dopant Si atoms would interact with these V_{Ga} that would lead to the formation of vacancy-interstitial complex defects such as V_{Ga}–Si_{Ga} [13, 17]. Within this Al content range (x = 10%–20%), (Al,Ga_{1−x})_{2}O_{3} films are single monolithic β-phase stable [3, 38], so our analysis recommends, in β-(Al,Ga_{1−x})_{2}O_{3}, Si doping is preferably occupying on Ga sites which may lead to the formation of complex V_{Ga}–Si_{Ga} defects due to the interaction with V_{Ga} vacancies.

The RDF for (Al,Ga_{1−x})_{2}O_{3} with x = 30%–50% are shown in figures 5(d)–(f). In figure 5(d), both Al and Ga BNC are higher as determined conclusively. In some cases, it is observed that from the origin (i.e. reference Si atoms at d = 0) towards a radially outward direction, BNC of Al is zero up to few nearest neighbor locations while BNC for Ga in locations surrounding d = 0 is higher (figure 5(e)). This result is similar to what was observed in the case of Al content, x = 10%–20% and suggests that Si is occupying on Ga sites. At d = 0, BNC for Ga drops significantly, suggesting V_{Ga} is present. However, there is another case when high Al concentration is observed in the immediate surrounding positions of the center Si atoms followed by BNC ∼ 0 for Ga up to few nearest neighbors indicating Al site occupancy of dopant Si atoms. BNC for Al at d = 0 is implying possibility of Al vacancy (V_{Al}) with which dopant Si would interact and form defect complexes [13, 17]. These contradictory results within Al content of x = 30%–50% layers indicate dopant Si atoms can occupy either Ga or Al site which can contribute to either V_{Ga}–Si_{Ga} or V_{Al}–Si_{Al} complex formation.

We believe, crystallinity degradation due to the presence of mixed (β + γ)-phases in (Al,Ga_{1−x})_{2}O_{3} at x = 30%–50% [22] is playing a pivotal role in such conflicting RDF results in these layers. Such phase segregation results in undetermined Al or Ga site occupancy of dopant atoms depending on these dopants are in the Al-rich or Al-depleted regions. It is reported in our previous work, that the (Al,Ga_{1−x})_{2}O_{3} layers with higher Al content, x = 60%–80% regains its single phase (γ-phase) crystalline structure [22]. The RDF analysis in these layers is illustrated in figures 5(g)–(i). From the RDF data, it is observed that surrounding the reference Si atoms up to few nearest neighbors, Al concentration is higher compared to Ga concentrations (BNC for Ga ∼ 0). This refers to Si is substituting on Al site. At the origin (d = 0; at reference Si) BNC for Al drops drastically. Our hypothesis is, at high Al content, since the formation energy of V_{Al} is lower [39], this kind of defects becomes dominant over V_{Ga} with which dopant Si atoms would interact. Similar phenomenon was observed in the case of AlGaN with high Al content (x > 60%) [16]. Within this Al range, dopant Si atoms are more likely to occupy on Al sites and interact with V_{Al} defects that leads to the formation of V_{Al}–Si_{Al} defect complexes [13, 17]. This specific cationic site occupancy by dopant Si contributes to the formation of cation specific defect complexes (V_{Al}–Si_{Al}) [40]. At low Al content (x < 0.30), such defect complexes are mostly V_{Ga}–Si_{Ga} which would drive the compensating knee (lower mobility because of reduced free electrons at high doping level) in (Al,Ga_{1−x})_{2}O_{3} films. On the contrary, V_{Al}–Si_{Al} complex defect would be the dominant one to govern the compensating effect in this film at high Al content (x > 0.50) that results in degraded device efficiencies [19]. The RDF analyses from individual (Al,Ga_{1−x})_{2}O_{3} layer presented in figure 5 were repeated in different regions and also for multiple data set acquired from several APT specimens of similar structures. A consistency in RDF results in multiple data set was verified at all Al content layers as presented in figures S5 and S6. It is noteworthy that, in these RDF results, the error bars are significant within the first few 0.1 nm from the center Si atoms at d = 0 which is mainly due to the statistical sampling errors possibly because of the small number of ions are involved [41]. With increasing the Al content along the (Al,Ga_{1−x})_{2}O_{3} layers, the contribution from the Al thermal tails to the Si peaks would be higher as evident from the increased background level with Al content (see table S1). This imposes challenges in the site occupancy analysis at high Al content layers if the Si peak is ranged randomly. However, with careful ranging of Si peaks, a consistency in site occupancy was observed over multiple volumes (as in figures 5, S5 and S6) at high Al content layers (x = 60%–100%). The issue of thermal tail contribution from Al into Si peaks in Si doped (Al,Ga_{1−x})_{2}O_{3} with high Al% could not be resolved due to the absence of peaks from minor Si isotopes. This may lead to some overestimation of Si counts if high Al content is present. To address this challenge, in the future, further optimization of laser energy will be performed on (Al,Ga_{1−x})_{2}O_{3} alloy with high Al% and site occupancy in the layers will be verified. The information reported here will be valuable for doping design in (Al,Ga_{1−x})_{2}O_{3} towards high performance devices.

4. Conclusion

We investigated the dopant interaction in Si doped (Al,Ga_{1−x})_{2}O_{3} films with varying Al content over a wide range of Al composition using APT. Moderate dopant density in the range of ∼10^{18} cm^{-3} with an almost uniform doping profile in (Al,Ga_{1−x})_{2}O_{3} layers was achieved when the Al content, x ≤ 0.50. At higher Al content of x ≥ 0.60, small Si segregations were observed which were attributed to the increased DX transitions of dopants or bond length differences of Al–O, Ga–O and Si–O at high Al content. In single phase β-(Al,Ga_{1−x})_{2}O_{3} crystalline layers (Al < 0.3), Si is found to occupy in Ga sites which could be contributing to the formation of V_{Ga}–Si_{Ga} defect complexes. When (Al,Ga_{1−x})_{2}O_{3} layers are of mixed phase (0.3 ≤ Al ≤ 0.5), Si prefers to occupy either Ga or Al cationic site. The reason could be attributed to the presence of different chemical phases in these layers that results in Al-rich or Al-depleted regions. On the contrary, at high Al content (Al ≥ 0.6) single phase γ-(Al,Ga_{1−x})_{2}O_{3} films, Si prefers to occupy in Al site instead
of Ga site. This Al site occupancy can account for the formation of $V_{\text{Al}}$–$S_{\text{Al}}$ complex arising from an increasing number of $V_{\text{Al}}$ sites. This specific cationic site occupancy by dopant Si would account for compensation knee (reduced mobility despite high doping level) resulting from the formation of cation specific III-defect complexes ($V_{\text{III}}$–$S_{\text{III}}$). This understanding of dopant behavior in Si doped ($\text{Al}_{x}\text{Ga}_{1-x}\text{O}_2$) films would be highly significant in terms of doping wide bandgap semiconductors for high power electronics as well as solar blind photodetectors.

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References

[1] Zhang F, Saito K, Tanaka T, Nishio M, Arita M and Guo Q 2014 Appl. Phys. Lett. 105 162107
[2] Oshima T, Okuno T, Arai N, Kobayashi Y and Fujita S 2009 Japan. J. Appl. Phys. 48 070202
[3] Krueger B W, Dandeneau C S, Nelson E M, Dunham S T, Ohuchi F S and Olimstead M A 2016 J. Am. Ceram. Soc. 99 2467
[4] Zhang Y et al 2018 Appl. Phys. Lett. 113 173502
[5] Vaidya A et al 2019 J. Appl. Phys. 126 095702
[6] Yuan S H, Wang C C, Huang S Y and Wu D S 2018 IEEE Electron Device Lett. 39 220
[7] Dong L, Jia R, Xin B, Peng B and Zhang Y 2017 Sci. Rep. 7 40160
[8] Hassa A, Wencskern H V, Vines L and Grundmann M 2019 ECS J. Solid State Tech. 8 Q3217
[9] Farzana E, Ahmadi E, Speck J S, Arehart A R and Ringel S A 2018 J. Appl. Phys. 123 161410
[10] Feng Z, Bhuivan A F M A U, Karim M R and Zhao H 2019 Appl. Phys. Lett. 115 256001
[11] Bhuivan A F M A U, Feng Z, Johnson J M, Chen Z, Huang H L, Hwang J and Zhao H 2019 Appl. Phys. Lett. 115 120602
[12] Ranga P, Rishinaramagalam A, Varley J, Bhattacharyya A, Feezell D and Krishnamoorthy S 2019 Appl. Phys. Express 12 111004
[13] Chichibu S F, Miyake H, Ishikawa Y, Tashiro M, Ohtomo T, Furusawa K, Hazu K, Hiramatuka K and Uedono A 2013 J. Appl. Phys. 113 213506
[14] Gogova D, Wagner G, Baldini M, Schmidbauer M, Irmscher K, Schewski R, Galazka Z, Albrecht M and Fornari R 2014 J. Cryst. Growth 401 665
[15] Chichibu S, Iwai A, Nakahara Y, Matsumoto S, Higuchi H, Wei L and Tanigawa S 1993 J. Appl. Phys. 73 3880
[16] Götz W, Johnson N M, Chen C, Liu H, Kuo C and Imler W 1996 Appl. Phys. Lett. 68 3144
[17] Uedono A, Tenjinbayashi K, Tsutsui T, Shimahara Y and Miyake H 2012 J. Appl. Phys. 111 013512
[18] Zhang Z, Farzana E, Arehart A R and Ringel S A 2016 Appl. Phys. Lett. 108 052105
[19] Harris J S, Baker J N, Gaddy B E, Bryan I, Bryan Z, Mirrielees K J, Reddy P, Collazo R, Sitar Z and Irving D L 2018 Appl. Phys. Lett. 112 152101
[20] Kelly T F, Larson D J, Thompson K, Alvis R L, Bunnel J H, Olson J D and Gorman B P 2007 Annu. Rev. Mater. Res. 37 681
[21] Pereira D, Arslan I and Liu J 2015 Nat. Commun. 6 7589
[22] Bhuivan A F M A U, Feng Z, Johnson J, Huang H L, Sarker J, Zhu M, Karim M R, Mazumder B, Hwang J and Zhao H 2020 APL Mater. 8 031104
[23] Thompson K, Lawrence D, Larson D J, Olson J D, Kelly T F and Gorman B 2007 Ultramicroscopy 107 131
[24] Sarker J, Broderick S, Bhuivan A F M A U, Feng Z, Zhao H and Mazumder B 2020 Appl. Phys. Lett. 116 152101
[25] Giddings A, Prosa T, Olson D, Clifton P and Larson D 2014 Microsc. Today 22 12
[26] Varley J B, Perron A, Lordi V, Wickramaratne D and Lyons J L 2020 Appl. Phys. Lett. 116 172104
[27] Blasco R, Ajay A, Robin E, Bougerol C, Lorentz K, Alves L C, Mouton I, Amici L, Grenier A and Monroy E 2019 J. Phys. D: Appl. Phys. 52 125101
[28] Devaraj A et al 2015 Nat. Commun. 6 6014
[29] Zhou J, Oqdqvist J, Thuvander M and Hedström P 2013 Microsc. Microanal. 19 665
[30] Schmidt J, Feng L, Poplawsky J D and Weckhuysen B M 2018 Angew. Chem., Int. Ed. 57 10422
[31] Moody M P, Gault B, Stephenson L T, Marcoux K R W, Powles R C, Ceguerra A V, Breen A J and Ringer S P 2011 Microsc. Microanal. 17 226
[32] Meher S, Rohjhirunsook T, Nandwana P, Tiley J and Banerjee J 2015 Ultramicroscopy 159 272
[33] Rademacher T, Al-Kassab T, Deges J and Kirchheim R 2011 Ultramicroscopy 111 719
[34] Gowtham S, Deshpande M, Costales A and Pandey R 2005 J. Phys. Chem. B 109 14836
[35] Ruiz J M, McAdon M H and Garcés J M 1997 J. Phys. Chem. B 101 1733
[36] Gault B, Müller M, Fontaine A L, Moody M P, Sharig A, Cerezo A, Ringer S P and Smith G D W 2010 J. Appl. Phys. 108 044904
[37] Haley D, Petersen T, Barton G and Ringer S P 2009 Phil. Mag. 89 925
[38] Kaun S W, Wu F and Speck J S 2015 J. Vac. Sci. Technol. A 33 041508
[39] Stampfl C and van de Walle C G 2002 Phys. Rev. B 65 155212
[40] Rass J (ed.) 2015 ‘III-Nitride Ultraviolet Emitters-Technology and Applications’ (Berlin: Springer)
[41] de Geuser F, Lefevbre W and Blavette D 2006 Phil. Mag. Lett. 86 227