Solubility limit and precipitate formation in Al-doped 4H-SiC epitaxial material

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Heavily Al-doped 4H–SiC structures have been prepared by vapor phase epitaxy. Subsequent anneals have been carried out in an Ar atmosphere in a rf-heated furnace between 1500 °C and 2000 °C for 0.5 to 3 h. Secondary ion mass spectrometry has been utilized to obtain Al concentration versus depth as well as lateral distributions (ion images). Transmission electron microscopy (TEM) has been employed to study the crystallinity and determine phase composition after heat treatment. A solubility limit of $\sim 2 \times 10^{20}$ Al/cm$^3$ (1900 °C) is extracted. Three-dimensional ion images show that the Al distribution does not remain homogeneous in layers heat treated at 1700 °C or above when the Al concentration exceeds $2 \times 10^{20}$ cm$^{-3}$. Al-containing precipitates are identified by energy-filtered TEM. © 2001 American Institute of Physics. [DOI: 10.1063/1.1402160]

High quality ohmic contacts require heavily doped SiC where doping levels close to the solubility limit are appreciated. If the solubility limit is exceeded, precipitates may form and the thermal stability and performance of SiC devices can be affected. For $p$-type ohmic contacts, heavily aluminum doped SiC is of prime interest. These highly doped layers can be prepared by ion implantation or during epitaxial growth taking advantage of site competition. $1$ Dopant incorporation during epitaxial growth is kinetic-controlled and solubility limits may be exceeded. The kinetic nature of Al incorporation can be elucidated by the anisotropy in “solubility limits” of $7 \times 10^{20}$ [(0001), silicon face] and $9 \times 10^{19}$ [(0001) carbon face] Al/cm$^3$ in sublimation grown 6H–SiC reported by Vodakov et al.$^2$ For postgrowth heat treatments, thermodynamic considerations have to be made. The thermal stability of heavily Al doped contact layers can be predicted from the ternary phase diagram Al–Si–C.$^{3–6}$ The three binary subsystems are well known with two intermediate phases, Al$_2$C$_3$ and SiC. Three ternary phases, Al$_3$SiC$_7$, Al$_5$SiC$_4$, and Al$_4$Si$_2$C$_5$ have been reported$^{3–7}$ but the stability of Al$_4$Si$_2$C$_5$ is questioned.$^3$ The chemical interaction between pure aluminum and SiC is well documented over a broad temperature range (room temperature up to 1600 °C),$^{4,5}$ but unfortunately, the SiC rich side, which is the area of interest for highly doped SiC layers, is not known in detail.

In this letter, we report on the solubility limit and precipitate formation in heavily Al doped epitaxially grown $p$-type 4H–SiC. After heat treatment, precipitate formation is observed in layers with Al concentration exceeding $2 \times 10^{20}$ cm$^{-3}$. Al concentration versus depth profiles as well as lateral distributions (ion images) have been measured by secondary ion mass spectrometry (SIMS). Transmission electron microscopy (TEM) has been utilized to investigate the crystal structure and determine phase compositions in the heavily doped SiC. Al doped 4H–SiC structures were prepared by vapor phase epitaxy at 1500 °C. The structure consists of five Al doped layers in the concentration range $2 \times 10^{19}$ to $3 \times 10^{20}$ cm$^{-3}$ separated by undoped material. A small variation in the Al concentration over the wafer is present. Subsequent heat treatments were performed in an Ar atmosphere in a rf-heated furnace according to a time and temperature schedule that varied from 0.5 to 3 h in duration and 1500 °C to 2000 °C. The aluminum depth distribution as well as lateral distributions (ion images) were measured by SIMS using a Cameca IMS 4f microanalyzer. A primary sputtering beam of 8.2 keV $^{32}$O$_2^+$ was applied and secondary $^{27}$Al$^+$ ions were detected. For depth profiling, the primary beam was rastered over an area of 200×200 μm$^2$ and the Al signal was recorded from the central part of this area ($\sim 60$ μm in di-
No diffusion is observed at the lowest level. Al diffusion is detected in four out of five samples annealed at 1700 °C, 1900 °C, and 2000 °C for 3 h, 2 h, and 2 h, respectively. Al diffusion starts at a level of about $10^{20}$ cm$^{-3}$ while a region with higher concentration, i.e., the as-grown concentration, remains in the center of the layer. If the annealing time increases, the region with the as-grown concentration is reduced and at long enough times, the concentration in the center of the fifth layer decreases. The outdiffusion is symmetric and the diffusion fronts are very abrupt with a shape diverging from a pure Fickian diffusion with no concentration dependence of the diffusion coefficient. In layer 5, the outdiffusion is detected in four out of five of the Al structures. No diffusion is observed at the lowest level (layer 1), but when the concentration increases, a remarkable increase in diffusion is revealed. The outdiffusion is symmetric and the diffusion fronts are very abrupt with a shape diverging from a pure Fickian diffusion with no concentration dependence of the diffusion coefficient. In layer 5, the outdiffusion starts at a level of about $2 \times 10^{20}$ cm$^{-3}$ while a region with higher concentration, i.e., the as-grown concentration, remains in the center of the layer. If the annealing time increases, the region with the as-grown concentration is reduced and at long enough times, the concentration in the center of the fifth layer decreases (not shown in Fig. 1). The same type of diffusion curves is obtained after heat treatment at 1700 °C to 2000 °C for 0.5 to 3 h. As long as the as-grown concentration remains in the center of layer 5, the level of outdiffusion does not change with time. No diffusion is detected at 1500 °C for 0.5 h. Diffusion curves of this kind indicate that the solubility limit has been exceeded and that precipitates may form. The level of outdiffusion can be interpreted as a solubility limit, in this case $\sim 2 \times 10^{20}$ Al/cm$^3$ (1900 °C). If the temperature is increased from 1700 °C to 2000 °C, the level of outdiffusion is increased by $\sim 30\%$.

A strong concentration dependence is observed for the Al diffusion. For instance, Fig. 1 shows four SIMS spectra of the $^{27}$Al depth distribution in an as-grown sample and after heat treatment at 1700 °C, 1900 °C, and 2000 °C for 3 h, 2 h, and 2 h, respectively. The as-grown Al concentration in layer 1 to 5 is 0.2, 1, 2, 3, and 3 multiplied by $10^{20}$ cm$^{-3}$, respectively. Al diffusion is detected in four out of five of the Al structures. No diffusion is observed at the lowest level (layer 1), but when the concentration increases, a remarkable increase in diffusion is revealed. The outdiffusion is symmetric and the diffusion fronts are very abrupt with a shape diverging from a pure Fickian diffusion with no concentration dependence of the diffusion coefficient. In layer 5, the outdiffusion starts at a level of about $2 \times 10^{20}$ cm$^{-3}$ while a region with higher concentration, i.e., the as-grown concentration, remains in the center of the layer. If the annealing time increases, the region with the as-grown concentration is reduced and at long enough times, the concentration in the center of the fifth layer decreases (not shown in Fig. 1). The same type of diffusion curves is obtained after heat treatment at 1700 °C to 2000 °C for 0.5 to 3 h. As long as the as-grown concentration remains in the center of layer 5, the level of outdiffusion does not change with time. No diffusion is detected at 1500 °C for 0.5 h. Diffusion curves of this kind indicate that the solubility limit has been exceeded and that precipitates may form. The level of outdiffusion can be interpreted as a solubility limit, in this case $\sim 2 \times 10^{20}$ Al/cm$^3$ (1900 °C). If the temperature is increased from 1700 °C to 2000 °C, the level of outdiffusion is increased by $\sim 30\%$.

After heat treatment at 1700 °C or above, the lateral Al distribution does not remain homogeneous in layers with Al concentrations above $2 \times 10^{20}$ cm$^{-3}$. Figure 2 shows SIMS images of a layer with $3 \times 10^{20}$ Al/cm$^{-3}$ after heat treatment at 2000 °C for 2 h. A higher Al concentration is displayed as a brighter region. In the ion images (a) and (b) the Al distribution in a $xy$ plane parallel to the surface is shown for the middle of the layer and at the outdiffused shoulder, respectively. In (c), data from 360 $xy$ images have been used to construct the $xz$ image. On top of the $xz$ image, the average Al concentration in each $xy$ image is plotted versus depth, the $z$ direction. In this case, a linear concentration scale is used.
atoms form Al containing precipitates with a size of 300 Å, homogeneously distributed, the Al intensity will average over the plane. These defects are three dimensional, with a preferential orientation along the $c$ axis. A track of defects was observed in layer 5. The extension of the defect in the $c$ direction coincides with for four unit cells of 4H–SiC.

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In conclusion, we have extracted a solubility limit of $2 \times 10^{20}$ cm$^{-3}$ (1900 °C) with a 30% increase from 1700 °C to 2000 °C for Al in 4H–SiC. Heat treatment at 1700 °C to 2000 °C of supersaturated Al doped 4H–SiC results in an inhomogeneous Al distribution due to Al containing precipitate formation. The precipitates have the preferential orientation of the $c$ axis in SiC. According to the ternary Al–Si–C phase diagram and the lattice structures a probable composition of the precipitating phase is Al$\text{Si}_2\text{C}_5$ although Al$\text{Si}_3\text{C}_3$ cannot be fully excluded from the HRTEM data.

FIG. 3. (a) Cross-sectional TEM image of heavily Al doped 4H–SiC after anneal at 2000 °C for 30 mins is shown. A track of defects is observed in the middle of the fifth Al layer (see Fig. 1). A preferential orientation of defects along the $c$ axis is observed. (b) Cross sectional HRTEM of one of the defects in (a) in the (1120) plane is shown. The extension of the defect in the (0001) direction coincides with for four unit cells of 4H–SiC.