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/cm³ (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 2×10^{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 7×10^{20} [(0001), silicon face] and 9×10^{19} [(0001) carbon face] Al/cm³ 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, Al₄C₃ and SiC. Three ternary phases, Al₈SiC₇, Al₄SiC₄, and Al₄Si₂C₅ have been reported³⁻⁷ but the stability of Al₄Si₂C₅ is questioned.³ The chemical interaction between pure aluminum and SiC is well documented over a broad temperature range (room tempera-

ture 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 2×10^{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 2×10^{19} to 3×10^{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 distribution (ion images) were measured by SIMS using a Cameca IMS 4f microanalyzer. A primary sputtering beam of 8.2 keV ³²(O₂)⁺ was applied and secondary ²⁷Al⁺ ions were detected. For depth profiling, the primary beam was rastered over an area of 200×200 μm² and the Al signal was recorded from the central part of this area (~ 60 μm in di-

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FIG. 1. SIMS profiles of the aluminum concentration versus depth for 4H-SiC samples are shown. Four samples are analyzed, one as grown and three annealed at 1700 °C, 1900 °C, and 2000 °C for 3 h, 2 h, and 2 h, respectively. Al diffusion decreases when the Al concentration decreases and no broadening of layer 1 is observed.

ameter). During ion image acquisition, a stack of 360 images was recorded. The primary beam (diameter $\leq 1 \mu\text{m}$) was rastered over an area of $25 \times 25 \mu\text{m}^2$ and the time of collecting data corresponds to a depth of $24 \text{ \AA}$ per image (i.e., the thickness of the image). High resolution transmission electron microscopy (HRTEM) was performed in a Philips CM20UT operated at 200 kV and a TECHNAI F30 ST FEG-TEM operated at 300 kV was employed for energy-filtered TEM (EFTEM).

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 of the 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 $2 \times 10^{20} \text{ cm}^{-3}$ 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 $\sim 2 \times 10^{20} \text{ Al/cm}^3$ (1900 °C). If the temperature is increased from 1700 °C to 2000 °C, the level of outdiffusion is increased by $\sim 30\%$.

FIG. 2. Ion image of the Al distribution obtained by SIMS is shown. The data is recorded in layer 5 of the sample heat treated at 2000 °C for 2 h shown in Fig. 1. 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.

After heat treatment at 1700 °C or above, the lateral Al distribution does not remain homogeneous in layers with Al concentrations above $2 \times 10^{20} \text{ cm}^{-3}$. Figure 2 shows SIMS images of a layer with $3 \times 10^{20} \text{ Al/cm}^3$ after heat treatment at 2000 °C for 2 h. A higher Al concentration is displayed as a brighter region in the images. The Al distribution is shown in two xy planes parallel and in one xz plane perpendicular to the sample surface [7° off from (0001) plane]. Data from 360 xy images have been used to construct the xz image. The lateral resolution in the xy plane is given by the diameter of the sputtering beam, typically $\leq 1 \mu\text{m}$. Frequent small structures, homogeneously distributed, may therefore not be resolved. In the z direction, the resolution is limited by the thickness of the ion images and/or the cascade mixing (as determined from Al δ layers), $24 \text{ \AA}$ and $25 \text{ \AA}$, respectively. In Fig. 2(c), the smallest resolvable structure in the z direction has the extension of three ion images. Furthermore, the Al concentration, in linear scale, versus depth is included in the xz image. The depth profile has been extracted as an average of the Al concentration in each xy plane. This profile is identical to the depth profile shown in Fig. 1 where the volume of

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 $\langle 0001 \rangle$ direction coincides with for four unit cells of 4H-SiC.

each data point was three times larger compared to the one used in the ion imaging.

HRTEM has been used to further investigate the crystal structure and in particular to determine if precipitates are formed. Cross sections were prepared from two samples, one as grown and one heat treated at 2000 °C for 30 min. No precipitates were detected in the as-grown sample and the lattice seems to be unaffected except for layer 5, where the lattice shows some evidence of stress. After heat treatment at 2000 °C, no disorder was revealed in the layers 1 to 4 while a 0.5 μm broad track of defects was observed in layer 5 [Fig. 3(a)]. These defects are three dimensional, with a preferential orientation along the c axes in SiC. In Fig. 3(b), a HRTEM image of one defect is displayed. The surrounding SiC lattice is not markedly influenced. A typical thickness of the structure is 40 Å and the extension in the c plane is in the range of 30 to 300 Å. If 1×10^{20} Al atoms mixed with 5×10^{22} Si atoms form Al containing precipitates with a size of $300 \times 300 \text{ Å}^2$, there will be about two precipitates/ μm^2 in the (0001) plane. This is close to the detection limit for SIMS ion images in the xy plane, since at higher precipitate densities, homogeneously distributed, the Al intensity will average out. The extension of the precipitates in the z direction in a SIMS xz image is similar to that deduced from HRTEM [Figs. 2 and 3(b)].

These results obtained by SIMS and HRTEM are further substantiated by EFTEM revealing that the precipitates are an Al containing phase. EFTEM also suggests a reduction of the Si concentration of the precipitates relative to the matrix. According to the ternary Al-Si-C phase diagram³ when the

solubility limit of Al in SiC is exceeded Al_4SiC_4 will most probably form. $\text{Al}_4\text{Si}_2\text{C}_5$ has also been identified as a possible candidate⁷ but its stability is doubtful and the compound has therefore not been included in the phase diagram. Keep in mind that if $\text{Al}_4\text{Si}_2\text{C}_5$ is stable, it will most likely be formed from a supersaturated solution of Al in SiC at thermodynamic equilibrium. Furthermore, the formation of Al_4C_3 during high dose ($3 \times 10^{17} \text{ cm}^{-2}$ and 350 keV) Al implantation at 500 °C has also been reported.⁸ If Al is introduced by ion implantation, the silicon to carbon ratio in SiC is conserved, this is not the case when the Al atoms are introduced during growth. Hence, different areas have to be considered in the phase diagram for ion implanted SiC and epitaxially grown material.

A hexagonal lattice can describe Al_4C_3 , Al_4SiC_4 , $\text{Al}_4\text{Si}_2\text{C}_5$, as well as 4H-SiC and their space groups have been identified as $R\bar{3}m$, $P6_3mc$, $R\bar{3}m$ and $P6_3mc$, respectively.⁷ According to the space groups there is a distinct possibility of aligning the c axis of all the aluminum containing carbides with the 4H-SiC lattice in a phase mixture. The extension in the c direction of two unit cells of Al_4C_3 (25 Å) coincides with five unit cells of 4H-SiC (10 Å). One unit cell of Al_4SiC_4 (22 Å) and $\text{Al}_4\text{Si}_2\text{C}_5$ (40 Å) coincides with two and four unit cells of 4H-SiC, respectively. The mismatch to 4H-SiC is negligible for Al_4C_3 and $\text{Al}_4\text{Si}_2\text{C}_5$ while a small mismatch is revealed for Al_4SiC_4 but not large enough to prevent epitaxial growth. Furthermore, the unit cells of Al_4SiC_4 and $\text{Al}_4\text{Si}_2\text{C}_5$ contain “layers” of Si-C with the same structure as in 4H-SiC and appear as a natural cross over between SiC and an aluminum containing phase.

In conclusion, we have extracted a solubility limit of $2 \times 10^{20} \text{ cm}^{-3}$ (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_4SiC_4 or $\text{Al}_4\text{Si}_2\text{C}_5$ although Al_4C_3 cannot be fully excluded from the HRTEM data.

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¹D. J. Larkin, P. G. Neudeck, J. A. Powell, and L. G. Matus, Appl. Phys. Lett. **65**, 1659 (1994).

²Y. A. Vodakov, E. N. Mokhov, M. G. Ramm, and A. D. Roenkov, *Amorphous and Crystalline Silicon Carbide III*, Springer Proc. Phys. Vol. 56, edited by G. L. Harris, M. G. Spencer, and C. Y. Yang (Springer, Berlin, 1992), p. 329.

³L. L. Oden and R. A. McCune, Metall. Trans. **18A**, 2005 (1987).

⁴J. C. Viala, P. Fortier, and J. Bouix, J. Mater. Sci. **25**, 1842 (1990).

⁵J. C. Viala, F. Bosselet, V. Laurent, and Y. Lepetitcorps, J. Mater. Sci. **28**, 5301 (1993).

⁶J. Gröbner, H. L. Lukas, and F. Aldinger, CALPHAD: Comput. Coupling Phase Diagrams Thermochem. **20**, 247 (1996).

⁷Z. Inoue, Y. Inomata, H. Tanaka, and H. Kawabata, J. Mater. Sci. **15**, 567 (1980).

⁸J. Stoemenos, B. Pécz, and V. Heera, Appl. Phys. Lett. **74**, 2602 (1999).