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Doping-induced strain and relaxation of Al-doped 4H-SiC homoepitaxial layers

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Aluminum-doped 4H-SiC epilayers with Al concentrations in the 7.4×10^{18} – 3.8×10^{20} cm⁻³ range were deposited on off-orientation (0001) wafers by chemical vapor deposition method and analyzed using high-resolution x-ray diffraction, transmission electron microscopy, and KOH etching. Reciprocal space maps of (0008) reflection revealed two distinct peaks originating from the substrate and doped epilayer. For Al concentration below 3.3×10^{20} cm⁻³, 10 μm thick layers were fully strained with the *a*-lattice parameter of the layer matching that of the substrate. The equilibrium *c*-lattice parameter change versus doping was determined to be $1.3 \pm 0.3 \times 10^{-24}$ cm³. The basal planes of the epilayers were tilted in respect to the substrate in the direction of the offcut with the tilt magnitude proportional to the doping concentration. The 10 μm thick layers with Al concentration above 3.3×10^{20} cm⁻³ underwent partial relaxation. The *a*-lattice parameter of the epilayer was higher than that of the substrate, the width of ω and 2θ scans of (0008) x-ray peaks broadened by a factor of 2 compared to strained layers, and the threading dislocation density increased by several orders of magnitude. Since no inclusions have been found in the relaxed epilayer, we interpret the above changes as due to strain relaxation by nucleation of dislocations. © 2004 American Institute of Physics. [DOI: 10.1063/1.1789627]

I. INTRODUCTION

Aluminum is commonly used as the shallow acceptor dopant in silicon carbide crystals and epilayers. Since the activation energy of substitutional aluminum is about 250 meV, it is necessary to use very high doping concentrations in order to produce low resistivity material and reduce the on-state losses in silicon carbide devices. At the same time, heavy Al doping of 4H-SiC is expected to cause lattice misfit between the epilayer and the substrate because of the difference in atomic radii between Al and Si. Whenever the Al-doped layer exceeds a critical thickness, it is expected to relax, inducing defect nucleation and a general degradation of material properties.

The experimental data on lattice parameter change with Al doping in 4H-SiC and 6H-SiC have been reported only by two groups^{1,2} while nitrogen doping of SiC has been studied by many groups.^{3–5} Tajima and Kingery¹ annealed mixed β-SiC and Al metal powders to prepare the SiC:Al material. The Al concentration in annealed samples, which was measured by emission spectroscopy, was in the 0.5×10^{20} – 3.5×10^{20} cm⁻³ range. X-ray powder diffraction scans showed linear increase of *c*-lattice parameter with Al-doping concentration and rate of increase of 1.0×10^{-24} cm³. However, the paper does not describe the structural characteristics of the material. For the sample preparation technique used in Ref. 1, one could expect nonuniform aluminum distribution in the SiC matrix and appearance of mixed polytypes induced by annealing.⁶ Kyutt, Mokhov, and Tregubova² analyzed sublimation grown 6H-SiC epitaxial layers doped during growth. The thickness of the epilayer was in the range of 1–150 μm.

Doping concentration, which was measured by neutron activation technique, ranged from 1.0×10^{19} to 6.0×10^{20} cm⁻³. The rate of *c*-lattice parameter increase with doping concentration was determined to be 0.8×10^{-24} cm³. However, the authors assumed all the epilayers were pseudomorphic, which at high doping levels, layer thicknesses, and deposition temperatures does not have to be the case. Such an assumption, if not correct, would lower the value of an equilibrium (unstrained) *c*-lattice parameter change.

The lattice misfit leads to generation of dislocations when the epilayer exceeds the critical layer thickness. Mathews and Blakeslee⁷ and People and Bean⁸ proposed two models that predict the theoretical critical layer thickness. The Mathews-Blakeslee approach was based on mechanical force balance while that of People and Bean on energy balance between strain and dislocation network formation. The estimates of the critical thickness vary between these two models by about two orders of magnitude. The experimental data on the onset of layer relaxation in Al-doped 4H-SiC would help to define the limit of doping concentrations and layer thicknesses beyond which high Al-doped SiC epilayers will begin to relax.

In this work, we focused on precise determination of the lattice parameter change versus doping and the onset of the strain relaxation in 4H-SiC:Al.

II. EXPERIMENT

The series of 10 μm thick Al-doped 4H-SiC epilayers were deposited by chemical vapor deposition on (0001)-oriented undoped semi-insulating 4H-SiC (8° offcut toward

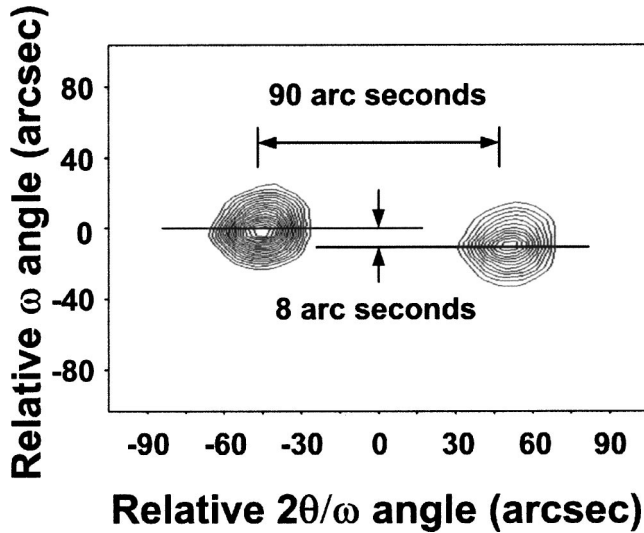


FIG. 1. The reciprocal space map for (0008) reflection of the 4H-SiC sample with $10\ \mu\text{m}$ thick epilayer ($N_{\text{Al}}=1.0\times 10^{20}\ \text{cm}^{-3}$) deposited on undoped substrate. The contours are plotted at 7% increments.

[11 $\bar{2}$ 0]). The growth conditions have been described in detail elsewhere.⁹ The Al-doping concentration of the epilayers was in the 7.4×10^{18} – $3.8\times 10^{20}\ \text{cm}^{-3}$ range as determined by secondary ion mass spectroscopy (SIMS). The lattice parameter change and tilt (misorientation) were measured by high-resolution x-ray diffraction using a Philips X'Pert MRD in triple-axis X-ray mode.¹⁰ The c -lattice parameters of epilayers and substrates and the tilt between epilayer and substrate were obtained from the nearly symmetric (0008) reflection, while a -lattice parameter was obtained using the asymmetric (10 $\bar{1}$ 7) reflections. The molten KOH etching at $500\ ^\circ\text{C}$ for 10 min was used to determine the dislocation density in strained layers. Similar information on relaxed layers was obtained by transmission electron microscopy (TEM) carried out on Philips EM420 and JEOL-2000. Plan-view and cross-section samples were prepared using standard procedures.

III. RESULTS AND DISCUSSION

A. Pseudomorphic layers

In samples with the doping concentration above $N_{\text{Al}}=2.5\times 10^{19}\ \text{cm}^{-3}$ two distinct peaks were observed in x-ray $2\theta/\omega$ diffraction scans. Figure 1 shows the representative reciprocal space map for (0008) reflection of the sample with $N_{\text{Al}}=1.0\times 10^{20}\ \text{cm}^{-3}$ by using triple-axis geometry. The incident beam was directed along [11 $\bar{2}$ 0] and opposite to the off-cut direction giving the incidence angle of 45.65° . The FWHM (full width at half maximum) of both peaks is about 20 arc sec for both ω and $2\theta/\omega$ directions. These values are typical of high quality silicon carbide crystals (such as Lely platelets) and indicate absence of low angle grain boundaries as well as low overall dislocation densities in the substrate and the epilayer. The reflections of the two peaks in Fig. 1 are separated along the 2θ axis by ≈ 90 arc sec, which shows that the c -lattice parameter of the epilayer is different from that of the substrate. Of the two peaks, the reflection from the epilayer is located at the smaller 2θ angle (on the left-hand

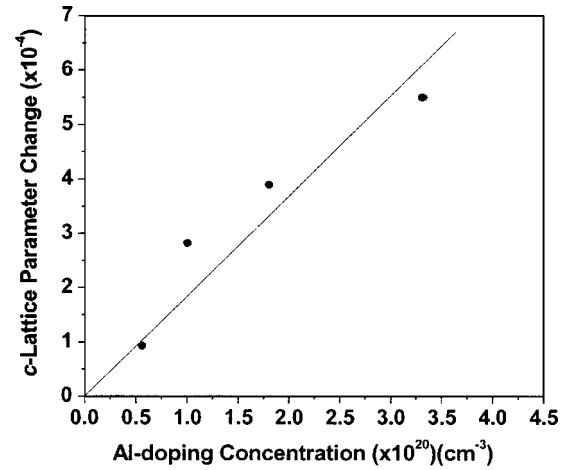


FIG. 2. c -lattice parameter change of 4H-SiC vs Al-doping concentration. Points represent experimental data. The line was obtained by the least squares fit.

side of Fig. 1). This assignment was determined based on measurements of relative peak intensities for (0004), (0008), and (00012) reflections. The Bragg angles (θ) for these reflections were 17.85° , 37.65° , and 66.75° , respectively. Accordingly, the x-ray penetration depth is increasing along this series and the substrate peak intensity should increase in relation to the epilayer peak. The shift of the epilayer peak toward a lower angle corresponds to increase of the c -lattice parameter value with aluminum doping. This result is in agreement with the previous observation of SiC:Al (Refs. 1 and 2) and the fact that the radius of Al ion ($r=1.26\ \text{\AA}$) is larger than that of Si ($r=1.17\ \text{\AA}$).¹¹

In addition to the shift in 2θ coordinate, Fig. 1 also shows that the two peaks are located at the slightly different ω values. The difference in the sample shown in Fig. 1 is ≈ 8.0 arc sec. This indicates that the basal planes of the epilayer are tilted in respect to the basal planes of the substrate. Since the relative ω position of the substrate peak in the off-cut direction is lower than that of epilayer peak, the epilayer is tilted in opposite direction to the offcut. The k -space maps of (0008) reflection collected with the wafer rotated by 90° (the ω axis of the diffractometer oriented parallel to the off-cut direction) did not detect any measurable tilt.

The experimental values of epilayer c -lattice parameter change as the function of aluminum concentration are shown in Fig. 2. The peak position of the epilayer changes linearly with aluminum content with the slope of $1.8\pm 0.7\times 10^{-24}\ \text{cm}^3$. For the samples below $N_{\text{Al}}=3.3\times 10^{20}\ \text{cm}^{-3}$ shown in Fig. 2, the threading dislocation density is about $5\times 10^4\ \text{cm}^{-2}$, which is a typical density found in high quality 4H-SiC substrates. The dislocations in the epilayers were, therefore, due to propagation of dislocations from the substrate as expected in homoepitaxy. FWHM of the epilayers is about 20 arc sec, which is also in consistent with high crystalline quality of the material. This leads us to conclusion that these epilayers are fully strained (or pseudomorphic).

From the experimental c -lattice parameter change of strained layers, one can calculate the values for the relaxed lattice parameters. Assuming a biaxial stress state in the ep-

ilayer, the relation¹² of the strains of ϵ_{ZZ} in the growth direction and ϵ_{XX} in the basal plane is given in the hexagonal system by

$$\frac{\epsilon_{zz}}{\epsilon_{xx}} = \frac{\frac{c_r - c_s}{a_r}}{\frac{c_r}{a_r - a_s}} = -\frac{2C_{13}}{C_{33}}, \quad (1)$$

where c_r and a_r are equilibrium (unstrained) lattice parameters of the Al-doped 4H-SiC and c_s and a_s are the values for the Al-doped film strained to match the undoped substrate. The value of a_s , the in-plane lattice parameter of the epilayer, is the same as that of the undoped 4H-SiC substrate used in this study. Similarly, c_o used below denotes the c -lattice parameter on the undoped 4H-SiC. C_{13} and C_{33} are the elastic stiffness constants of 4H-SiC.¹³ When the doped epilayer is fully relaxed:¹²

$$\frac{\epsilon_{zz}}{\epsilon_{xx}} = \frac{\frac{c_r - c_o}{a_r - a_o}}{\frac{c_r}{a_r}} = \frac{C_{11} + C_{12} - 2C_{13}}{C_{33} - C_{13}}, \quad (2)$$

where C_{11} and C_{12} are the elastic stiffness constants of 4H-SiC.¹³ The c_s , c_o , a_s , and a_o were obtained from x-ray experiments and c_r and a_r are the only unknown values in the above equations. Combining Eqs. (1) and (2) the relaxed c -lattice parameter (c_r) and a -lattice parameter (a_r) can be obtained from the following equations:

$$c_r = \frac{a_r c_s}{\left(1 + \frac{2C_{13}}{C_{33}}\right) a_r - \frac{2C_{13}}{C_{33}} a_s}, \quad (3)$$

$$a_r = \frac{\frac{2C_{13}}{C_{33}} c_o a_s + \frac{C_{11} + C_{12} - 2C_{13}}{C_{33} - C_{13}} c_s a_o}{\left(\frac{C_{11} + C_{12} - 2C_{13}}{C_{33} - C_{13}} - 1\right) c_s + c_o + \frac{2C_{13}}{C_{33}} c_o}. \quad (4)$$

The slope (β^{expt}) of the equilibrium c -lattice parameter change obtained from the Eqs. (3) and (4) versus doping is calculated to be $1.3 \pm 0.3 \times 10^{-24} \text{ cm}^3$. This value is more than 30% higher than the values published in Refs. 1 and 2 and we believe is more accurate due to higher crystalline quality of the structures and precise calibration of the SIMS measurements.

The experimentally determined value of β^{expt} can be compared to the lattice parameter change calculated based on the size difference. Jacobson *et al.*⁵ have discussed the dopant size effect (β^{size}) on 4H-SiC lattice parameters doped with nitrogen and we have adopted their approach. Assuming the atomic radii of silicon and aluminum of 1.26 and 1.17 Å, respectively, the lattice parameter change ($\beta_{\text{calc}}^{\text{size}}$) is $1.1 \times 10^{-24} \text{ cm}^3$. The lattice parameter change obtained from the quasicontinual model¹⁴ also is about $1.0 \times 10^{-24} \text{ cm}^3$.

The difference between calculated value and the experimental one reported here can be due to the deformation potential of the band edge occupied by the free holes.¹⁵ The

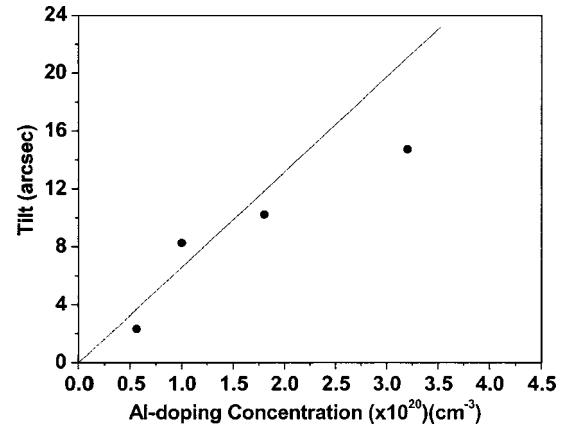


FIG. 3. Degree of tilt between the basal planes of epilayer and the substrate vs Al-doping concentration. Points correspond to experimental tilt angles with line obtained from the formula (7) and experimental values of lattice misfit.

total lattice parameter change can be expressed as the sum of the size effect and the deformation potential contribution:

$$\beta^{\text{total}} = \beta^{\text{carrier}} + \beta^{\text{size}}. \quad (5)$$

Cardona and Christensen¹⁶ suggested the contribution of the free holes in the following form:

$$\beta^{\text{carrier}} = a_{c,v}/3B, \quad (6)$$

where β^{carrier} is the free hole-induced lattice strain, $a_{c,v}$ is the hydrostatic deformation potential of the valence band, and B is bulk modulus. By fitting our experimentally obtained β^{expt} , we have estimated the value of deformation potential (a_v) at 0.37 eV. At this point in time, neither experimental nor theoretical values for the deformation potential in 4H-SiC are available in order to compare with this estimate. One can use the value calculated for the cubic polytype, which was obtained by two different approaches at 4 and -1 eV.¹⁷ The error in either one of these calculations was on the order of few eV. Our experimental value is within this error.

In many systems the lattice misfit is known to cause the tilt (misorientation) between the epilayer and the substrate.¹⁸⁻²⁴ Two models^{18,19} have explained such tilt, one of which by Nagai¹⁸ applies to pseudomorphic growth. The tilt magnitude is given by a formula:¹⁸

$$\tan \alpha = \tan \epsilon (\Delta d/d), \quad (7)$$

where α , ϵ , and $\Delta d/d$ are tilt angle, off-cut angle, and lattice parameter difference between epilayer and the substrate along the growth direction, respectively. Figure 3 shows the experimental tilt angles obtained from the reciprocal space maps on strained Al-doped epilayers. The values of tilt were calculated using known 8° off-cut angle and experimental values of $\Delta c/c$. The calculated results, which are based on the tilt angles of the pseudomorphic layers, are plotted as a straight line in Fig. 3. It is apparent that the effect suggested by Nagai agrees well with the experimental results for aluminum concentration up to $3.0 \times 10^{20} \text{ cm}^{-3}$. The last point corresponding to the relaxed layer falls markedly below the predicted value.

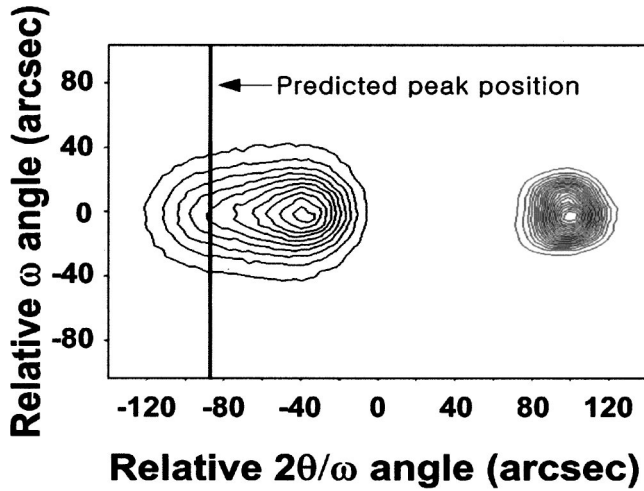


FIG. 4. The reciprocal space map for (0008) reflection of the sample with $10\ \mu\text{m}$ thick epilayer ($N_{\text{Al}}=3.8\times 10^{20}\ \text{cm}^{-3}$) deposited on undoped substrate.

B. Relaxation

The reciprocal space maps of layers with aluminum concentration above $3.3\times 10^{20}\ \text{cm}^{-3}$ have different characteristics from those shown in Fig. 1. An example of a (0008) reflection obtained on the layer with $N_{\text{Al}}=3.8\times 10^{20}\ \text{cm}^{-3}$ is shown in Fig. 4. First, the FWHM of the epilayer is 45 arc sec, which is approximately twice the value of the substrate peak and strained epilayers shown in Fig. 1. The peak broadening is likely due to random strains induced by high dislocation density characteristic of relaxed heteroepitaxial layers, resulting in the decrease of the epilayer peak intensity. The integrated peak intensity ratio $I_{\text{epilayer}}/I_{\text{substrate}}$ is ≈ 1.5 in relaxed layer and equal to that of pseudomorphic layers. Second, the epilayer peak is located closer to the substrate peak than what is expected from the experimental dependence for strained layers in Fig. 2 and the aluminum concentration determined by SIMS. These characteristics led us to believe that the difference is due to strain relaxation. The presence of relaxation was confirmed by the measurement of the a -lattice parameters of the substrate and epilayer in asymmetric (10 $\bar{1}7$) reflection. The a -lattice parameter of the epilayer shown in Fig. 4 is $\approx 0.025\%$ higher than that of the substrate.

The calculated critical layer thicknesses by using Matthews and Blakeslee's model⁷ and People and Bean's model⁸ using lattice misfit of 4.0×10^{-4} corresponding to the $N_{\text{Al}}=3.3\times 10^{20}\ \text{cm}^{-3}$, Burger's vector of $b=\frac{1}{3}\langle 11\bar{2}0 \rangle$, and Poisson's ratio of 0.213 (Ref. 25) are about 0.4 and 200 μm , respectively. The experimental value discussed above is $\approx 10\ \mu\text{m}$.

The dislocation density and distribution in all samples were assessed by molten KOH etching and TEM. In strained layers (shown in Figs. 1 and 2) the typical dislocation density was $5\times 10^4\ \text{cm}^{-2}$. The dislocations in the epilayers were, therefore, due to propagation of dislocations from the substrate as expected in homoepitaxy. However, the dislocation density in the sample shown in Fig. 4 was significantly higher. Figure 5(a) shows a plan-view TEM image along

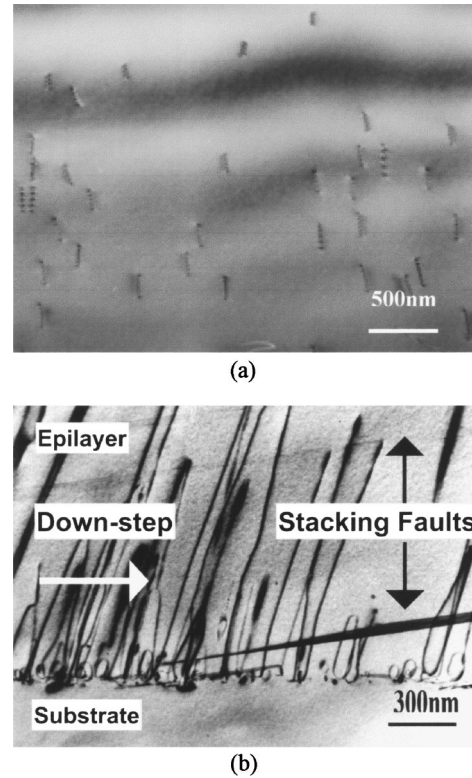


FIG. 5. (a) Plan-view TEM image of the epilayer doped with $N_{\text{Al}}=3.8\times 10^{20}\ \text{cm}^{-3}$. The short lines correspond to threading dislocations with estimated density of $5\times 10^8\ \text{cm}^{-2}$. (b) Cross-sectional TEM image of the same epilayer showing the epi/substrate interface.

[0001] zone axis of the epilayer with $N_{\text{Al}}=3.8\times 10^{20}\ \text{cm}^{-3}$. The image shows multiple short dislocation segments with the direction close to but inclined in respect to the c axis. All dislocations show a characteristic oscillatory contrast reported, for example, by Marukawa.²⁶ The sample was thinned from the substrate side and the observed dislocation density was determined close to the surface of the $10\ \mu\text{m}$ thick epilayer. The dislocation density was $\approx 5\times 10^8\ \text{cm}^{-2}$, which is about four orders of magnitude higher than that of the strained layers. Figure 5(b) shows the cross-sectional TEM image of the same sample. The threading dislocations are visible as loops originating at the epilayer and substrate interface and are inclined at the angle of about 20° to the layer surface. All threading dislocations are inclined in the same "down step" direction corresponding to the step flow direction during epitaxy. This effect was suggested to be due to image force exerted on the dislocation by the macrosteps on the epilayer surface.²⁷ Figure 5(b) also shows the presence of stacking faults in the heavily Al-doped epilayers appearing as lines inclined by 8° to the epi/substrate interface. The morphology of these faults and their origin will be discussed in a separate publication. It is worth noting that none of the TEM samples examined showed the presence of second phase inclusions related to high aluminum content. This indicates that even the $3.8\times 10^{20}\ \text{cm}^{-3}$ of Al concentration is still below the solid solubility limit in SiC at the growth temperature of $1500\ ^\circ\text{C}$. The degradation of epilayer quality is induced by stress relaxation rather than formation of aluminum carbide precipitates.

IV. CONCLUSIONS

We report the buildup of strain with increasing doping concentration in heavily aluminum-doped 4H-SiC epilayers and the onset of strain relaxation. The critical epilayer thickness for Al content of $3.3 \times 10^{20} \text{ cm}^{-3}$ was estimated to be below $10 \mu\text{m}$. Strain relaxation occurs through the nucleation of dislocation half loops.

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