Demonstration of *p*-type 3C–SiC grown on 150 mm Si(100) substrates by atomic-layer epitaxy at 1000°C

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The potential for enhancement of Si-based devices by growth of SiC films on large-diameter Si wafers is hampered by the very high temperatures (close to the Si melting temperature) that are needed for growth and doping by the existing techniques. Here, we present a unique doping method for growth of Al-doped single-crystalline 3C–SiC epilayers on 150 mm Si(100) substrates by atomic-layer epitaxy at 1000 °C using a conventional low-pressure chemical vapor deposition reactor. Al atomic concentration in the range of 2.8×10^{19} to $2.1 \times 10^{20} \text{ cm}^{-3}$, proportional to the supply volume of trimethylaluminium, is experimentally demonstrated. A doping mechanism, based on the supply sequence of precursors and reactor pressure, is proposed.

Keywords: A1. Crystal morphology, A1. X-ray diffraction, A3. Chemical vapor deposition processes, B1. Silicon carbide, B2. Semiconducting materials.

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1. Introduction

Commercially available 6H-SiC and 4H-SiC substrates are very expensive and small in area. Comparatively, 3C-SiC is the only polytype that can be epitaxially grown on cheap and large diameter Si substrates, which is suitable for integration with well-established Si processes. In terms of device fabrication, SiC films with different doping types and concentrations are urgently needed. Although intensive investigation on the heteroepitaxial growth of 3C-SiC on Si substrate was carried out using atmospheric/low-pressure chemical vapour deposition (APCVD/LPCVD) at substrate temperatures around 1350 °C or higher by simultaneous supply of Si-containing and C-containing sources [1–9], most of this work was focused on unintentionally doped films. Very limited work has been devoted to *p*-type doping in 3C-SiC films deposited on Si, which remains limited to deposition processes that require temperatures (around 1350 °C) close to the Si melting temperature [8,9]. Such high temperatures are not suitable for most applications because of dopant redistribution in the Si substrate and severe wafer bow due to accumulated thermal-mismatch stress at the SiC/Si heterojunction. To minimize these effects, alternating-supply/atomic-layer epitaxy (ASE/ALE) was developed, which reduced the growth temperature of unintentionally doped 3C-SiC films to around 1000 °C [10–17]. This relatively low temperature not only reduces the dopant redistribution in the Si substrate, but also reduces wafer bow; measured wafer bow of 2.1 µm for a prime grade 150 mm Si(100) wafer increased to 3.1 µm after 960 nm of SiC deposition [10]. However, up to date, there is no published report on *p*-type doped 3C-SiC films grown by ASE/ALE method at similar temperatures. Boron (B) and aluminium (Al) are the two possible *p*-type dopants in SiC. Compared with B, Al has relative shallower acceptor level and is much less influenced by hydrogen incorporation during chemical vapour deposition

(CVD) growth [18–20]. In this paper, we present a novel *in-situ* doping method for growth of Al-doped 3C–SiC epilayers on 150 mm Si(100) substrates by ALE at 1000 °C. Since the doping is carried out at atomic-layer level, very sharp junction profiles can be achieved compared with doping by diffusion [21].

2. Experimental details

The growth of Al-doped 3C–SiC on on-axis 150 mm *n*-type Si(100) substrates was performed at 1000 °C in a hot-wall LPCVD reactor. The employed precursors were silane (SiH₄, 99.9994%), acetylene (C₂H₂, 99.9999%), and trimethylaluminium [(CH₃)₃Al, TMAI]. The details about Si surface activation and carbonization steps are published elsewhere [10]. The epitaxial growth of Al-doped 3C–SiC was performed cycle by cycle using ALE method, each cycle consisted of the following five steps: 1) supply of SiH₄ for 10 s with a flow rate of 2.0 standard cubic centimetre per minute (sccm); 2) pump out for 30 s; 3) supply of TMAI (0.1 sccm) for 10 to 20 s; 4) supply of 1.5 sccm C₂H₂ and 0.1 sccm TMAI for 10 s; and 5) pump out for 30 s. The growth rate was controlled at 0.61 ± 0.02 nm/cycle. Microstructure analyses of the epitaxial layers were performed using x-ray diffractometry (XRD) and transmission electron microscopy (TEM). The θ – 2θ locked XRD scans were performed with CuK α radiations using a Bruker D8 advance x-ray diffraction system, the acquisitions being from 30° to 95° with an increment of 0.005°/step and a duration of each step of 0.5 s. The rocking curve scans were performed with an increment of 0.002°/step and a duration of each step of 0.5 s. The TEM measurements were carried out on cross-section specimens using an FEI Tecnai F30 TEM (operating at 300 kV). Film thickness was measured by a Nanometrics NanoSpec/AFT (model: 200, assuming a refractive index of 2.65). The surface topography was observed by atomic force

microscopy (AFM, model: MFP3D-BIO), the operating mode being air tapping and the radius of curvature of the cantilever tip being 10 nm. Secondary ion mass spectroscopy (SIMS) was employed to investigate Al atomic concentration. The relative sensitivity factor (RSF) of Al was calculated based on three depth profiles on the same standard Al-doped SiC sample with known Al concentration, and then this RSF was employed to characterize the Al-doped samples studied in this paper. The conductivity type and carrier concentrations were characterized by hot-probe and Hall effect techniques.

3. Results and discussion

3.1 Characterization of crystal morphology and microstructure of Al-doped SiC

Al-doped 3C-SiC films of thicknesses of 290, 620 and 990 nm were grown with 20 s TMAI supply in step 4 in the previously listed sequence of steps. Applying the standard 9 points method for Nanospec-based measurement of thickness variation across a wafer, it was found that the thickness nonuniformity was controlled with $\pm 1\%$. The root mean square (RMS) roughness, measured by AFM in an area of $5 \times 5 \mu\text{m}^2$, was found to be 13.75 nm for 290 nm thick Al-doped SiC (shown in Fig. 1). This roughness is much smaller than the roughness of unintentionally doped SiC films grown with same supply volume of C_2H_2 and is comparable to that of unintentionally doped SiC grown with much higher supply volume of C_2H_2 (10 s with a flow rate of 10 sccm) [10]. The parameters influencing the surface roughness need to be investigated further for Al-doped SiC films.

Fig. 1. AFM image in an area of $5 \times 5 \mu\text{m}^2$ for 290 nm Al-doped SiC.

The orientation and crystal quality of the grown SiC films on Si(100) substrates were characterized by XRD. For a 990 nm Al-doped SiC film grown on a Si substrate (the locked XRD θ - 2θ scan is shown in Fig. 2), 3C-SiC(200), 3C-SiC(400), and Si(400) diffraction peaks were detected, indicating that epitaxial 3C-SiC films are grown on Si(100) substrate. The same results were also obtained for SiC films with a thickness of 290 and 620 nm. The intensities of 3C-SiC(200) and (400) diffraction peaks increase with increasing film thickness and the full-width at half-maximum (FWHM) of 3C-SiC(200) diffraction peak decrease from 0.31° (290 nm epilayer) to 0.24° (620 nm epilayer) and to 0.22° (990 nm epilayer). Rocking curve scans of the 3C-SiC(200) diffraction peak also demonstrate a continuous reduction of FWHM, from 1.20° to 0.72° and 0.68° , which indicates that the crystal quality is improved with the increase in film thickness. By comparing the FWHM data of the rocking curves for unintentionally doped and Al-doped SiC [10], it was found that the crystal quality is comparable (Al doping did not cause any observable deterioration of crystal quality).

Fig. 2. XRD θ - 2θ locked scan of 990 nm Al-doped 3C-SiC on Si(100) substrate.

A cross-sectional TEM image of 290 nm Al-doped 3C-SiC film observed along the [110] direction of electron incidence is shown in Fig. 3. It can be seen that the defect density is reduced with increasing distance from the interface. The interface remains quite smooth and no etch pits were observed. However, delamination occurred during the sample preparation. The selected area electron diffraction (SAED) from both the SiC film and Si substrate observed along the [110] direction is shown in Fig. 4, which demonstrates that single-crystalline 3C-SiC is epitaxially grown on Si substrate.

Fig. 3. Cross-sectional TEM image of Al-doped 3C-SiC/Si observed along the [110] direction of electron incidence.

Fig. 4. SAED of 290 nm 3C–SiC grown on the Si(100) substrate observed along the [110] direction of electron incidence.

3.2 Al concentration and doping mechanism investigation

SIMS was employed to investigate the atomic concentration of Al in the epitaxially grown SiC films. Two samples with different doping concentrations were prepared by varying the supply time of TMAI with a constant flow rate of 0.1 sccm. Sample SiC_10s TMAI was grown with 10 s supply of TMAI for each cycle, which resulted in Al atomic concentration in the range of 2.8 to $5.2 \times 10^{19} \text{ cm}^{-3}$. Sample SiC_20s TMAI was grown with 20 s supply of TMAI for each cycle, which resulted in Al atomic concentration in the range of $8.9 \times 10^{19} \text{ cm}^{-3}$ to $2.1 \times 10^{20} \text{ cm}^{-3}$. These SIMS results are shown in Fig. 5 as plots of Al atomic concentration versus sputtering depth (SiC thickness is 260 nm for both samples). It can be clearly seen that Al atomic concentration increased with supply time of TMAI for each cycle. The slight increase in Al atomic concentration during the growth period, which is observed for both samples, indicates that there is a small history effect of TMAI.

Fig. 5. Al atomic concentration versus sputtering depth measured by SIMS.

Hot-probe and Hall-effect techniques were employed to characterize the conductivity type and carrier concentration. For all the Al-doped 3C–SiC films grown on *n*-Si substrates, a positive voltage reading on a cold probe with respect to a hot probe (the hot probe was grounded) indicated that the films are of *p* type conductivity. Furthermore, the sign of the measured Hall voltage also confirmed that Al-doped SiC is *p* type conductive.

To act as effective *p*-type dopants, it is believed that Al atoms occupy Si sites in SiC crystal lattice [22]. Al also acts as a *p*-type dopant in Si films. The total-energy calculations for adsorption of Al atoms on Si surface predicted the formation of Al dimers and Al–Si bonds [23]. Therefore, the following doping mechanism is proposed. With the supply of SiH₄, the Si atoms that are adsorbed on the SiC surface arrange themselves in self-assembled pattern, these Si atoms are only few atomic-layer thick and usually believed to present in reconstruction states [11,12,15]. This pattern is formed during SiH₄ supply and remains in place during the subsequent pump out period. When TMAI is supplied, Al atoms are adsorbed at the Si-terminated surface (Al–CH₃ bonds break below 527°C [24]). It is most likely that the adsorbed Al atoms form both Al–Al dimers and Al–Si bonds [23] (there is no evidence to show whether an Al atom would replace a Si atom that sits on a proper lattice site). Some of the carbon atoms contributed by TMAI would also adsorb on the Si-terminated surface and form Si–C bonds [24]. The high vacuum during each growth cycle and the presence of pump out periods are important to provide adequate pressure and time for adsorbed atoms to be accommodated in those favorable positions. Finally, the supply of C₂H₂ enables the adsorbed Si and Al atoms to be converted into SiC layers. With this, one cycle of growth is completed. With the partial pressure of TMAI studied in this paper, the adsorption of Al atoms on Si-terminated surface is not expected to be self-limited but to be proportional to the total supply volume of TMAI, which is why sample SiC_20s TMAI has higher Al atomic concentration than sample SiC_10s TMAI.

The room-temperature carrier concentration, obtained by Hall effect measurements, is $1.6 \times 10^{17} \text{ cm}^{-3}$ for sample SiC_10s TMAI (no proper Hall effect measurement could

be performed on sample SiC_20s TMAI due to high current leakage through the heterojunction). The room-temperature film resistivity, measured by a standard four-point probe technique, is $0.31 \text{ } \Omega \cdot \text{cm}$ for sample SiC_10s TMAI. Based on the measured values for the carrier concentration and the film resistivity, the hole mobility is $126 \text{ cm}^2/\text{V} \cdot \text{s}$, which is higher than typical values reported in open literature [8,9]. The temperature dependence of conductivity of sample SiC_10s TMAI (from 300 to 370 K) is shown in Fig. 6. It can be seen that the film conductivity reduces with increasing temperature, which is inconsistent with the effect of incomplete ionization that would be expected for a deep acceptor level. The conductivity–temperature dependence, presented as a log-log plot, is linear with the slope of $-3/2$. This type of conductivity–temperature dependence is observed when the carrier concentration is constant with temperature and the carrier mobility is dominated by phonon scattering which is the case of standard *p*-type layers in Si technology. However, the possible assumption of constant carrier concentration would require an adequate explanation for the fact that the measured carrier concentration is less than 1 % of the total Al atomic concentration. Clearly, the measured electrical characteristics of this film require further investigation. A possible line of investigation is to consider the impact of background impurities (such as nitrogen and oxygen) and structural defects (including antisite atoms and vacancies) that could act as compensating *n*-type dopants.

Fig. 6. Temperature dependence of conductivity of sample SiC_10s TMAI. Both axes are log scales.

4. Conclusions

In conclusion, we have experimentally demonstrated that *p*-type single-crystalline 3C–SiC films can be grown on Si substrates at as low temperature as 1000°C. The doping element is aluminium and the growth technique is atomic-layer epitaxy that is implemented in a conventional low-pressure chemical vapor deposition reactor. Crystal quality of Al-doped 3C–SiC film, as revealed by x-ray diffraction and transmission electron microscopy, is similar to that of unintentionally doped film. SIMS measurements of Al atomic concentration versus depth showed that Al atomic concentration ranged from 2.8×10^{19} to $2.1 \times 10^{20} \text{ cm}^{-3}$, proportional to the total supply volume of trimethylaluminium. Both hot-probe and Hall effect measurements confirmed that the Al-doped SiC are of *p*-type conductivity. The following doping mechanism is proposed: first, Si atoms are adsorbed on SiC surface and arrange themselves into a stable structure, then the supply of TMAI enables Al atoms to adsorb to Si-terminated surface, and finally the arrival of C_2H_2 converts the adsorbed Si and Al atoms into Al-doped 3C–SiC.

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Figure captions

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Figures

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