Growth of cubic SiC thin films on Si(001) by high vacuum chemical vapor deposition using 1,3-disilabutane and an investigation of the effect of deposition pressure

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Up to now, it is common to grow the cubic SiC thin films on Si substrates heteroepitaxially by chemical vapor deposition (CVD) at above 1000 °C using separate Si and C sources such as silane or chlorosilane and various hydrocarbon gases.8–10 Sometimes high growth temperatures result in high tensile stress and crystalline lattice defects in the as-grown SiC films due to the difference in thermal expansion coefficients between SiC and Si. Such defects and strain in the heteroepitaxial films can degrade carrier mobilities and increase leakage junction currents. Moreover, the use of separate sources in the growth of SiC films may result in some deviations in stoichiometry, leading to point defects and inclusions.11 Therefore, it is highly desirable to grow 3C-SiC films on Si substrates at lower temperatures for device integration, and to employ sources that are not toxic and pyrophoric and possibly containing both silicon and carbon in a same molecule to reduce the activation barrier of SiC formation. The use of single molecular precursor that contains silicon and carbon atoms in the same molecule to reduce the activation barrier of SiC formation is a material with whose excellent thermal properties and wide band gap make it a potentially important candidate for high-temperature, high-voltage, and high-power device applications.1–4 More recently, SiC is being considered for applications in the microelectromechanical systems area for applications such as high temperature microsensing and as a microactuator since similar devices based on Si lack high-temperature capabilities with respect to both electrical and mechanical properties.5,6 However, the highly stable nature of single crystalline semiconductors cannot be used for the cubic SiC(3C-SiC or β-SiC) because it easily transforms into the hexagonal type SiC(α-SiC) above 1600 °C and dissociates at 2830 °C.7 Therefore, high purity and high quality bulk single crystalline 3C-SiC produced by sublimation and liquid phase epitaxial growth is not commercially available in sizes above 2 in. Moreover, high quality single crystalline substrates sufficiently lattice-matched to SiC to produce a defect-free material are not also available. Thus, epitaxial growth of cubic SiC films on Si substrates is highly desirable, since single crystalline 3C-SiC films can easily be obtained on Si substrates despite the ~20% lattice mismatch between SiC and Si.

I. INTRODUCTION

Silicon carbide (SiC) is a material with whose excellent thermal properties and wide band gap make it a potentially important candidate for high-temperature, high-voltage, and high-power device applications.1–4 More recently, SiC is being considered for applications in the microelectromechanical systems area for applications such as high temperature microsensing and as a microactuator since similar devices based on Si lack high-temperature capabilities with respect to both electrical and mechanical properties.5,6 However, the highly stable nature of single crystalline semiconductors cannot be used for the cubic SiC(3C-SiC or β-SiC) because it easily transforms into the hexagonal type SiC(α-SiC) above 1600 °C and dissociates at 2830 °C.7 Therefore, high purity and high quality bulk single crystalline 3C-SiC produced by sublimation and liquid phase epitaxial growth is not commercially available in sizes above 2 in. Moreover, high quality single crystalline substrates sufficiently lattice-matched to SiC to produce a defect-free material are not also available. Thus, epitaxial growth of cubic SiC films on Si substrates is highly desirable, since single crystalline 3C-SiC films can easily be obtained on Si substrates despite the ~20% lattice mismatch between SiC and Si.

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We have deposited cubic SiC thin films on Si(001) substrates by high vacuum chemical vapor deposition (CVD) using a single molecular precursor of 1,3-disilabutane (DSB) at various temperatures (600–1000 °C) and pressures in the range of 1 × 10^-6–1 × 10^-3 Torr. A single-crystalline cubic SiC thin film with stoichiometric composition can be obtained under deposition conditions of 900–1000 °C and 4.0–6.5 × 10^-6 Torr. However, on increasing the deposition pressure and decreasing the growth temperature to 1 × 10^-5 Torr and 600 °C, respectively, the film became polycrystalline. The effect of deposition pressure on the film growth rate and crystallinity was also studied. Based on the experimental results from x-ray diffraction, x-ray photoelectron spectroscopy, scanning electron microscopy, transmission electron microscopy, and transmission electron diffraction, the best SiC film was grown at 900 °C and 6.5 × 10^-6 Torr of DSB at a maximum growth rate of 0.1 μm/h. The thicknesses of as-grown films were determined by cross-sectional SEM and Rutherford backscattering spectroscopy. Two different activation energies for cubic SiC film formation were obtained from Arrhenius plots. The deposition temperatures and pressures used in this study are lower by as much as 200 °C and a factor of 10^2, respectively, compared with those grown by conventional CVD methods. © 2003 American Vacuum Society. [DOI: 10.1116/1.1585073]
temperature on the growth rate and film crystallinity to understand the influence of deposition parameters and to identify initial film growth mechanism. The advantage of the high vacuum (less than $1 \times 10^{-5}$ Torr) CVD method is that it allows us to make high quality SiC thin films with very smooth surfaces and without oxygen impurities.

II. EXPERIMENT

The experiment was carried out in a homemade high vacuum CVD system. The substrate used in this study was Si(001), cut into a square of $12 \times 12$ mm$^2$. The substrate needs to be properly cleaned and prepared for the deposition to avoid residual surface impurities that can create defects in the growing films. Prior to introducing the Si substrates into the CVD chamber, it was initially treated by a chemical cleaning process similar to the method proposed by Ishizaka and Shiraki$^{17}$ to remove contamination and form a thin oxide layer on the surface. Before deposition the substrate was heated to 850 °C and kept at this temperature for about 20 min to remove the protective oxide layer. The temperature of the substrate was measured with an optical pyrometer. The substrate was measured to be 400 Torr at room temperature. It needs to be properly cleaned and prepared for the deposition handling system under high vacuum ($<$2.0 $\times 10^{-7}$ Torr) conditions and was further purified by freeze-pump-thaw cycles using liquid nitrogen. SiC thin films were deposited directly on the clean Si(001) surface without the carbonization process and carrier gas was passed at varying temperatures (600–1000 °C) and pressures such as high vacuum conditions (1.0–8.0 $\times 10^{-6}$ Torr). The duration of deposition was about 2–6 h, and the growth rate changed depending on the experimental conditions. The as-grown 3C-SiC films were characterized with x-ray diffraction (XRD), x-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), transmission electron microscopy (TEM), transmission electron diffraction (TED), and Rutherford backscattering spectroscopy (RBS).

III. RESULTS AND DISCUSSIONS

To check whether the deposition temperature and pressure are major parameters or not to influence the film crystallinity, we first grew SiC thin films on Si(001) substrates by 1,3-disilabutane at various temperatures between 700 and 1000 °C and a fixed pressure (6.5 $\times 10^{-6}$ Torr) for the same time (6 h), and then measured their x-ray diffraction patterns as shown in Fig. 1. In Fig. 1, we can see that the film crystallinity improves with increasing growth temperature. Below 800 °C [see Figs. 1(a) and 1(b)], a SiC film of polycrystalline nature was obtained, and an amorphous type SiC film was grown at 600 °C. However, above 900 °C only a single sharp diffraction peak due to the cubic structure of the SiC film appeared at $2\theta = 41.4°$ for 3C-SiC(002) and $2\theta = 90.0°$ for (004) reflections, respectively. No other diffraction peaks except those attributable to the Si substrates were detected. This indicates that single-crystal SiC films were epitaxially deposited on Si substrates below 1000 °C. This deposition temperature is lower by as much as 200 °C compared to conventional ones, and the film growth temperature can be one of major film deposition parameters to control the film quality.

In order to understand the effect of deposition pressure on crystallinity more systematically, we also carried out the deposition of SiC thin films at different pressures and the fixed temperature of 900 °C for 6 h. Figure 2 shows the XRD patterns obtained from the as-grown films at the pressure range of $1 \times 10^{-6}$–8 $\times 10^{-5}$ Torr, respectively. As shown in Fig. 2, the intensity of the diffraction peaks increased with increasing deposition pressure, suggesting a high growth rate with the higher flux of precursor. Moreover, Fig. 2(e) shows that a number of diffraction peaks due to the reflections from 3C-SiC(111) and 3C-SiC(220) planes were observed at $2\theta = 35.6°$ and 60.0°, indicating polycrystalline film formation at growth pressure above $8 \times 10^{-6}$ Torr. Therefore, we can conclude that the highest quality SiC film confirmed by XRD, RBS, TEM, TED, and XPS was obtained under the deposition condition of 900 °C and 6.5 $\times 10^{-6}$ Torr, and the growth temperature and pressure are main parameters influencing both film crystallinity and deposition rate.

Figure 3 shows a typical high-resolution XP spectra of Si 2p and C 1s for the SiC thin films grown at various temperatures. In Fig. 3(a), the Si 2p spectra (99.0 eV) appearing below 450 °C show similar shapes with the absence of any C 1s contribution due to SiC crystalline formation, indicating no strong reaction between the precursor and the substrate takes place until 450 °C. However, the full width at half maximum of the Si 2p XP peak becomes broader and broader with increasing substrate temperature from room
temperature to 450 °C, suggesting randomly oriented thin SiC cluster formation on the Si(100) surface. This trend can distinctly be seen at the data of 600 °C of which the Si 2p curve component is related to a more silicon-rich region (its lower binding energy denoting Si atoms bonded to fewer carbon atoms than in SiC). In the case of SiC thin films grown above 700 °C, the SiC component becomes dominant, signifying a strongly increased SiC thickness which attenuates or causes the disappearance of the Si substrate contribution. This result indicates that the Si 2p peak [Fig. 3(a)] at 100.6 eV and the C 1s peak [Fig. 3(b)] at 282.7 eV correspond to the SiC phase. The Si:C ratio measured by their high-resolution XP spectra was 1.0 ± 0.02 for the SiC films obtained under the growth conditions in the range of 700–1000 °C and of 1.0–6.5 × 10⁻⁶ Torr. The details of an in situ XPS study on temperature effects have already been published elsewhere.¹⁸

Figure 4 shows the SEM images of SiC thin films grown on Si(100) at 900 °C and various deposition pressures. This figure shows clearly the changes of surface morphology of the 3C-SiC films with various pressures between 2 × 10⁻⁶ and 8 × 10⁻⁶ Torr. From Fig. 4 we also know that the size of SiC crystals was increased whenever we increased the flux of precursor (i.e., deposition pressure), indicating that pressure will strongly affect the film growth rate and even crystallinity. The smoothest surface can be obtained at lower deposition pressure of 2 × 10⁻⁶–8 × 10⁻⁶ Torr. However, the film grown under low pressure has a low growth rate, yielding very thin film layers as measured with cross-sectional SEM and confirmed with ellipsometry. The typical film thickness and deposition rates for as-grown SiC films are 1800 Å and 300 Å/h at 700 °C, increasing to 6000 Å and 1000 Å/h in the temperature range of 800–900 °C, and then decreasing up to 1000 Å and 200 Å/h at 1000 °C, respectively. The optimum deposition condition of our high vacuum CVD process was therefore kept at 900 °C and 6.5 × 10⁻⁶ Torr and were of high quality as shown by XRD and TED data, with good stoichiometry and quite smooth surfaces with submicron-size crystals. However, as shown in Fig. 5(a) the film growth rate obtained from the as-grown SiC films at 900 °C with different pressures was found to be proportional to deposition pressure over the range from 1.0 × 10⁻⁶ Torr to 8.0 × 10⁻⁶ Torr. We have reported previously the general tendency of the changes in surface morphology on 3C-SiC films grown at various temperatures from 700 to 1000 °C under the same deposition pressure of 6.5 × 10⁻⁶ Torr for 6 h.¹⁸ The surface morphologies of the films grown between 900 and 950 °C show better crystallinity and a smoother surface than the films grown between 700 and 800 °C. It is believed that as the substrate temperature is increased to 900 °C, the surface roughness increases whereas the crystal size also increases, indicating improvement of crystal quality. However,
by increasing the temperatures from 900 to 1000 °C the surface roughness is decreased drastically and the film is transformed to a monocrystalline structure. In conclusion, growth temperature and pressure are very important factors in the attainment of single crystallinity in the films. TEM and TED verify these effects very clearly.

Figure 5 shows typical cross-sectional TEM images of the 3C-SiC films grown on Si(001) at various deposition temperatures from 700 to 900 °C and pressures of 2.0 × 10⁻⁶ Torr and 6.5 × 10⁻⁶ Torr, respectively. Polycrystalline crystals can be seen in both Figs. 5(a) and 5(b) when the growth temperature is kept at 700 °C. However, for low deposition pressure relatively high quality films with smooth surfaces and sharp interfaces were obtained relative to those grown at high pressure.

The inserts of Figs. 5(a) and 5(b) show selected area transmission electron diffraction patterns of the same SiC films. As the deposition pressure increases, the crystal size as well as grain size also increases, and broad spot patterns containing rings were also observed, indicating the coexistence of single crystalline and polycrystalline SiC crystals. When the film growth temperature is increased, much better SiC films of a monocrystalline nature and large grain sizes relative to those grown at low temperature can be observed from Figs. 5(c) and 5(d). The spots seen in the TED patterns of Figs. 5(c) and 5(d) are due to cubic SiC film formation; the inner strong spots correspond to the Si substrate, and the outer weak spots to 3C-SiC. Besides the major diffraction spots, the weak extra spots may be due to twinned crystals in the film layers. The contrast seen in the cross-sectional view...
TEM micrographs [see also Figs. 5(c) and 5(d)] is believed to be associated with mass contrast due to surface roughness and/or misoriented or twinned regions surrounding the epitaxial growth, which is similar to the films grown by CVD. However, the critical temperature for similar results on Si(001) was approximately near 900 °C.

The dependence of film growth rates (or thicknesses) on deposition pressure and temperature was also studied. The SiC film growth rates were obtained by the changes of film thickness. Figure 6(a) shows a distinct behavior of the pressure effect that reflects a strong dependency of the film growth rate on the flux of precursor. The growth rate, as shown in Fig. 6(a), increased exponentially with increase in flux. This tendency is not so much affected by the growth temperature due to a predominant deposition mechanism such as diffusion controlled process between 800 and 900 °C. However, Fig. 6(b) shows a different variation of growth rates as a function of deposition temperatures. Two distinct growth temperature regions are apparent, that is, the growth rate increases rapidly with deposition temperature in the range of 600–800 °C. This behavior is characteristic of a kinetically controlled deposition process in which the surface decomposition of the precursor is the rate determining step. The activation energy for the SiC film deposition calculated from the slope of the Arrhenius plot is about 67.4 kJ/mol. In the higher temperature region over 800 °C, however, a negative activation energy of −158.2 kJ/mol was obtained, indicating that the growth rate is controlled by the mass transport of reagents through the boundary layer to the growth surface. This is termed the region of diffusion controlled growth and possibly some portion of desorption and/or prereaction, reacted with CO or residual gases in the CVD system, during thin film growth.

The RBS measurements were performed using 2.24 MeV 4He++ particles at normal incidence. A good depth resolution is achieved using a scattering angle of 165°. Both film quality and interface misfit of layers were checked with channeling along the [001] direction. The last direct evidence
of the crystallographic quality of the deposits is given by RBS channeling. Figure 7(a) presents a comparison between the random RBS and channeling spectra for a typical SiC thin film with a 1200-Å-thick film grown at 900 °C and 6.5 × 10⁻⁶ Torr. A very low minimum backscattering yield, \( \chi_{min} \), which is the ratio of the minimum counts between the aligned and random RBS spectra, 0.843 is obtained, suggesting a relationship between \( \chi_{min} \) and growth temperatures [Fig. 7(b)]. As growth temperature increases, the \( \chi_{min} \) is decreased, signifying that a film with good crystallinity can be produced at high deposition temperature.

IV. CONCLUSIONS

We have successfully grown the cubic SiC thin films on Si(001) substrates under the deposition conditions of temperature in the range of 600–1000 °C and pressures of 1.0–8.0 × 10⁻⁶ Torr using a single molecular precursor of 1,3-disilabutane and a high vacuum CVD method. In addition, we have also studied in the effects of deposition pressure and temperature in the growth rate and film crystallinity to understand the influence of deposition parameters and film growth mechanism. The optimum deposition condition of the formation of epitaxial single crystalline 3C-SiC thin films confirmed by XRD, XPS, SEM, and TEM, and TED was found to be 900–950 °C and 2.0–6.5 × 10⁻⁶ Torr. XPS and RBS also show that the SiC films grown at above 700 °C have stoichiometric composition. Two distinct growth temperature regions are apparent, that is, the growth rate increases rapidly with deposition temperature in the range of 600–800 °C, and an activation energy for the SiC film deposition was obtained to be 67.4 kJ/mol. This behavior is characteristic of a deposition process as kinetically controlled deposition in which the surface decomposition of the precursor is the rate determining step. However, in the higher temperature region over 800 °C a negative activation energy −158.2 kJ/mol was also obtained, indicating that the growth rate is controlled by the mass transport of reagents through the diffusion controlled reaction. Furthermore, we can see a distinct pressure effect on the growth rate within our experimental condition.

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