Low-temperature epitaxial growth of cubic SiC thin films on Si(111) using supersonic molecular jet of single source precursors

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Abstract

Epitaxial cubic SiC thin films have been deposited on Si(111) by supersonic molecular jet epitaxy of the single source precursors of methylsilane (MS), CH\textsubscript{3}SiH\textsubscript{3}, and dimethylsilane (DMES), (CH\textsubscript{3})\textsubscript{2}SiH(CH\textsubscript{3}CH\textsubscript{2})\textsubscript{2}, at temperatures in the range 780–950°C. Single crystalline, crack-free epitaxial cubic SiC thin films were successfully grown on carbonized Si(111) substrates at temperatures as low as 830°C using MS and DMES. Highly oriented cubic SiC thin films in the [111] direction were obtained on uncarbonized Si(111) substrates at 780°C using MS and at 950°C from DMES. However, the growth temperature of DMES was lowered to 830°C on Si(111) when the substrates were initially carbonized with a supersonic jet of acetylene. Below 780°C, moreover, only polycrystalline cubic SiC thin films were grown on either carbonized or uncarbonized Si(111) surfaces with MS. The advantage of supersonic molecular jets of the single source precursors employed in this study is evident in that the surface carbonization process may not be necessary, and the deposition procedure is quite simple and safe to handle. Real-time, in situ optical reactivity was used to monitor the film growth. The as-grown films were characterized in situ by Auger electron spectroscopy (AES) and ex situ by ellipsometry, SEM, FTIR, UV/Visible spectroscopy, and XRD (especially omega and phi-scan measurements). © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

Silicon carbide (SiC) attracts a growing interest on account of its properties making it suitable for high-power, high-frequency, and high-temperature devices [1]. SiC is known to occur in a large number of hexagonal and rhombohedral modifications and one cubic modification called the β-(cubic) form. In all of the forms of SiC each atom of one kind has four nearest neighbors of the other kind at the regular tetrahedral positions [2]. The Si-C distance is always 1.89 Å. The cubic SiC has the zincblende structure with one SiC molecule per unit cell, and can be grown on Si substrates unlike other polytypes.

Heteroepitaxial growth of cubic SiC films on Si substrate has been known to be difficult due to the large mismatches of lattice parameter (20%) and the thermal expansion coefficients (8%) between cubic SiC and Si. The two-step CVD method was proposed to relax the mismatches by the introduction of a buffer layer [3], and cubic SiC was grown epitaxially on Si(100) by the two-step CVD method using a hydrocarbon-SiH\textsubscript{4}-H\textsubscript{2} gas system [4–6]. The buffer layer formed by reacting Si(100) substrate with the hydrocarbon-H\textsubscript{2} gas system was identified to be single crystalline cubic SiC (3C-SiC) with stacking faults and small grains (10 nm) with small angle misorientations [7,8]. However, the best crystal quality and purity is usually obtained at relatively high temperature of 1300°C for deposition on Si substrate. Moreover SiH\textsubscript{4}, although an important chemical for SiC growth, is an extremely hazardous and pyrophoric compound that requires high safety requirements. So an increase in safety and a reduction in growth temperature is desired for the wide application of practical devices.

Recently there have been some reports on attempts to grow SiC under less hazardous conditions. One way to go is to choose alternative precursors with Si-C bonds, which allow lower temperatures and exclude the extremely pyrophoric SiH\textsubscript{4} from the process. Hence alkylsilanes, such as hexamethyldisilane [9,16], diethylsilane [10], 1,3-disilabutane [11], methylsilane [12], silacyclobutane [13], and t-butylmethylsilane [14] have produced single crystalline layers of high quality SiC at atmospheric pressure or low
pressure (<5 Torr). In order to obtain epitaxial cubic SiC films at low temperatures, moreover, ways must be considered to enhance the surface migration of the physically adsorbed species and also to perform the reaction of SiC crystallization at suitable sites on the substrate. For this purpose, it seems that the use of supersonic molecular jet epitaxy (SMJE) is effective. Previously, we have reported the validity of the use of supersonic molecular jet epitaxy using single source precursors [14,15].

In this paper, we will describe the growth process and low temperature epitaxy of cubic SiC thin films on silicon substrates using single source precursors of methylsilane and dimethylethylsilane by the SMJE method.

2. Experimental

The experiments were carried out in an UHV chamber, which has a base pressure of $1 \times 10^{-9}$ Torr. A home-made molecular beam apparatus with a nozzle (orifice diameter: 150 μm) was attached to the first introduction chamber and the main growth chamber for carbonization and high-pressure film growth with the supersonic jets, respectively. A more detailed description is given elsewhere [14,15].

The substrate (20 × 20 mm size) used in this study was n-type Si(111) (boron doped, 9.0–17.0 Ω-cm) and was initially prepared by chemical cleaning processes using acetone, isopropylalcohol, 48% HF solution and deionized water. After the samples were inserted into the chamber, they were mildly annealed by a BN heater with a supersonic jet of hydrogen at 650°C for 1 h, and then were annealed at 950°C for about 15 min just prior to carbonization and deposition. Clean surface was confirmed in situ using Auger electron spectroscopy (AES). The carbonization and deposition temperatures were monitored by K-type chromel-alumel thermocouple and by an infra-red pyrometer. The general condition of growth pressures and temperatures for the carbonization process and SiC growth were $1 \times 10^{-3} – 5 \times 10^{-7}$ Torr and 780–850°C depending on the nozzles and precursors used in this study. The commercially available single molecular precursors used in this study were methylsilane (MS), CH₃SiH₃, 5% mixed with hydrogen, and dimethylethylsilane (DMES), (CH₃)₂SiH₂CH₂SiH₂CH₃. Freeze-pump-thaw cycles were employed for purification, and the QMS was used to verify the purity of these precursors. Due to quite high vapor pressure of the precursor itself, there was no need to heat the precursor and nozzle. Hydrogen gas was used as a carrier and a bubbler gas. Acetylene gas was used for the surface carbonization of the substrates.

The growth rate was measured in situ by monitoring the intensity changes of a He/Ne laser beam (wavelength: 633 nm) reflected from the surface of the growing films. The as-grown films were characterized ex situ by ellipsometry, XRD, FTIR, X-ray ϕ(ϕ)-scan and optical transmission measurements.

3. Results and discussion

3.1. Growth of cubic SiC thin films on Si(111) from methylsilane

Epitaxial growth was monitored by real-time, in situ optical reflectivity where oscillations provide information on the growth rate and the surface roughness. During SiC film growth, oscillations as shown in Fig. 1, took place because of the interference effect of light in the transparent SiC film. This method made in situ monitoring of the growth rate possible. Assuming a refractive index of 2.7 for SiC, consistent with previous measurements on stoichiometric SiC [9,16], the deposition rate could be estimated in real time, and the deposition runs could be terminated at any arbitrary film thickness. The film thickness should be calculated from the wavelength of the laser and the index of refraction, but the situation is complicated by the non-uniform film thickness. More accurate growth rates were calculated using the results of film thickness measurements obtained by ellipsometry and alpha-step profile. Fig. 1 shows an oscillation curve of optical reflectivity with a period dependent intensity changes which were monitored in-situ and in real-time from a growing thin film on Si(111) at 780°C. The SiC deposition rate obtained from Fig. 1 was 0.1 μm/h for 1 × 10⁻⁴ Torr MS and hydrogen mixture. With increasing deposition time, however, the amplitude of the oscillations was reduced implying that the surface was roughening. Furthermore, the growth rate increased to 0.17 μm/h with increasing substrate temperature to 830°C. Usually, in this study, the surfaces of as-grown films were mirror-like with some haze. However, with increasing deposition temperatures, the surface close to the center of the substrate was often dull gray and appeared rougher than...
Fig. 2. XRD patterns of epitaxial cubic SiC thin films grown on carbonized Si(111) substrates with methylsilane at (a) 780°C and (b) 830°C. (Insets show X-ray rocking curves of the same samples).

the edges. Moreover, there were also some pits near the center of the film surface. This indicates that the surface turned rougher and darker at high temperatures. The insert of Fig. 1 shows optical transmission taken through a SiC membrane grown under the same deposition condition as Fig. 1 and then fabricated by etching away 1/4 inch diameter of the Si substrate. The data shows that the onset of transmission is about 230 nm.

Using X-ray diffraction, the crystallinity of the films was quickly confirmed. From the X-ray θ-2θ diffraction spectra of films grown at 780°C (Fig. 2a) and 830°C (Fig. 2b) on carbonized Si(111) surfaces using supersonic MS molecular jet obtained by a scanning from 25 to 60°, we note the presence of a strong peak at ~35° satisfying the Bragg diffraction for (111) planes of the SiC film layer. For the film grown at 780°C, shown in Fig. 2a, a broad and strong peak at about 35.6° with weak and small shoulder peak was observed due to (111) reflection of cubic SiC indicating a polycrystalline film with a small grain size. This means that, even if the proper buffer layer was formed, it is difficult to obtain a good epitaxial film on both carbonized and uncarbonized Si(111) substrates at 780°C using the MS and hydrogen mixture. In this study, therefore, only highly oriented cubic SiC thin films in the (111) direction were obtained on either carbonized or uncarbonized Si(111) substrates with MS at temperatures between 780 and 830°C. Below 780°C, moreover, very thin polycrystalline cubic SiC thin films were grown on either carbonized or uncarbonized Si(111) surfaces with MS. However, when the growth temperature was increased to 830°C after carbonization of the acetylene supersonic jet only, monocrystalline, crack-free epitaxial cubic SiC thin films were obtained on Si(111) with MS. In the spectrum from the 830°C film, shown in Fig. 2b, only two peaks can be observed, one corresponding to the Si(111) substrate and the other corresponding to the SiC(111) film. Therefore, it is obvious from Fig. 2a,b that the crystallinity improves as a higher growth temperature is utilized. The insets of Fig. 2 show X-ray rocking curves (Ω-scan) of corresponding films with FWHMs of Δω = 5.30° for 780°C film and Δω = 2.0° for 830°C film. The results of Ω-scan and θ-2θ scan measurements show that FWHM of the SiC(111) peaks as the cubic SiC films became larger as the film is grown at lower growth temperatures indicating poor film quality. It might be due to an ease of secondary nucleation on any plane except the (111) of cubic SiC.

From the X-ray diffraction spectra, however, it is not possible to determine if the epitaxial films are truly single crystalline or highly (111) textured polycrystals. For this purpose, φ-scan measurements are helpful to reveal the real crystalline state of the SiC film since φ-scan are a semiquantitative measure of the depth-averaged concentration of defects and strain in the film. The φ-scans were used to measure in-plane structural order and the diffractometer was set up to detect diffraction from the (220) family of planes as the SiC(111) film was rotated about its surface normal. Fig. 3 show the X-ray φ-scans of the cubic SiC films grown on carbonized Si(111) with a supersonic molecular jet of MS at 780°C (Fig. 3a) and 830°C (Fig. 3b). Both data give a periodic diffraction symmetry which is consistent with single crystallinity. The periodicity of the diffraction peaks, every 60°, indicates a highly oriented SiC crystal in the zincblende structure. The main difference in both data case is a peak width, due to different growth temperature and crystal quality. For Fig. 3a obtained from a SiC film grown at 780°C, there are much broader peaks with shoulder
Fig. 4. Auger electron spectra of epitaxial cubic SiC thin films grown on carbonized Si(111) substrates with methylisilane at (a) 780°C and (b) 830°C.

growth temperature the sample becomes stoichiometric within the resolution of the measurement method. The AES data can explain the results of optical transmission measurements. As shown in Fig. 1, we obtained a low optical transmittance from a SiC film grown at 780°C with MS. The inset of Fig. 1 shows poor optical property with 50% transmittance in the UV range due to excess carbon in the SiC film. However, the inset of Fig. 5, obtained from a film grown at 830°C, shows good optical property with 80% transmittance. This is in agreement with the AES results (Fig. 4b) possibly reflecting the higher degree of crystallinity of the as-grown films. FTIR experiments on films grown on carbonized Si(111) surfaces permit the direct verification of the presence of SiC, whereas on thick films it permits the evaluation of their quality. The IR absorption data of Fig. 5 obtained from the same samples as mentioned above show a strong absorption peak around 794 cm⁻¹ due to the Si-C stretching vibration in SiC film. However, the samples grown at temperatures lower than 780°C have smaller peak intensities and wider FWHM than those grown at high temperature with about the same thickness. The broad absorption peak indicates that the SiC film formation at low temperature can be limited by a low rate of surface thermal reaction of the precursor on Si.

3.2. Growth of cubic SiC thin films on Si(111) from dimethylethylsilane

Growth of cubic SiC film on carbonized Si(111) substrate at 830°C using DMES gives only the SiC(111) diffraction peak, shown in Fig. 6a, hence the crystals are highly oriented with parallel epitaxy, with respect to the substrate. Fig. 6a shows the X-ray θ-2θ diffraction pattern of epitaxial cubic SiC thin film grown on carbonized Si(111) surface by a supersonic molecular jet of DMES at 830°C and 1 × 10⁻⁵ Torr for 5 h. The thickness of this film is approximately 1.0
peaks indicating that the film is single crystalline zincblende SiC(111) and is comparable with Fig. 3b obtained from SiC film which grew at 830°C using MS. This indicates that nearly the same quality of SiC film can be obtained under the similar deposition conditions using both MS and DMES.

In the case of SiC using DMES, it is also possible to grow the cubic SiC films on uncarbonized Si(111) surfaces directly. However, only thin films of polycrystalline cubic SiC in the thickness range 0.2–0.4 μm were obtained on uncarbonized Si(111) substrates from DMES under the same growth condition. The growth of SiC films with the same thickness as that grown on carbonized Si(111) has been obtained at 950°C. This means that the growth temperature of DMES was lowered to 830°C on Si(111) when the substrate were initially carbonized at 850°C with a supersonic jet of acetylene. Noticeably, however, the film grown on the uncarbonized substrate resulted in a more uniform morphology than that on carbonized surface. The advantage of supersonic molecular jets of the single source precursors employed in this study is evident in that the deposition procedure is quite simple and safe to handle, and the surface carbonization process may not be necessary to obtain more uniform SiC films.

4. Conclusions

Cubic SiC thin films have been grown by supersonic molecular jet epitaxy of single source precursors on Si(111) substrates at temperatures in the range 780–950°C. Monocrystalline, crack-free epitaxial cubic SiC thin films were successfully grown on carbonized Si(111) substrates using a supersonic molecular jets of MS and DMES at 830°C. Highly oriented cubic SiC thin films in the (111) direction were obtained on uncarbonized Si(111) substrates at 780°C using MS and at 950°C from DMES, respectively. However, the growth temperature of DMES was lowered to 830°C on Si(111) when the substrates were initially carbonized with a supersonic jet of acetylene. Below 780°C, moreover, only polycrystalline cubic SiC thin films were grown on either carbonized or uncarbonized Si(111) surfaces with MS. The advantage of supersonic molecular jets of the single source precursors employed in this study is evident in that a higher growth rate can be obtained under high vacuum deposition condition, and the deposition procedure is quite simple and safe to handle. Real-time, in situ optical reflectivity was used to monitor the film growth. The as-grown films were characterized in situ by AES and ex situ by ellipsometry, XRD, FTIR, X-ray φ(φ)-scan and optical transmission measurements. The film's crystallinity measured by the FWHM of the X-ray rocking curve, X-ray φ(φ)-scan and FTIR is improved by increasing the deposition temperature. To the best of our knowledge, this is the first report of cubic SiC film growth using DMES by the supersonic molecular jet epitaxy.
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