Growth of Cubic SiC Films Using 1,3-Disilabutane

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Cubic SiC films have been grown on the Si(100) and Si(111) substrates in the temperature range 650–900 °C by low-pressure organometallic chemical vapor deposition (LP-OMCVD) using 1,3-disilabutane, $H_3SiCH_2SiH_2CH_3$, as a single molecular precursor. Polycrystalline cubic SiC films were formed on Si(100) substrates at such a low temperature as 650 °C. The films obtained on carbonized Si(100) substrates at temperatures higher than 850 °C show improved crystallinity in their X-ray diffraction patterns. On the other hand, highly oriented SiC films in the [111] direction were formed on carbonized Si(111) substrates at 900 °C. The growth temperatures in this study are much lower than those previously reported, and this is the first report of cubic SiC films grown using 1,3-disilabutane.

Introduction

Silicon carbide (SiC) is an interesting semiconductor material with applications to electronic and optoelectronic devices due to its excellent thermal stability and wide-bandgap energy.[1,2] Moreover, silicon carbide is especially attractive for high-temperature, high-power, high-frequency, and high-radiation operating devices, since its saturated electron drift velocity, breakdown electric field, thermal conductivity, and tolerance to ionizing radiation are significantly superior to those of Si and GaAs.[3,4] Silicon carbide is also known as a material which crystallizes in various crystalline structures or polytypes. Among many polytypes of silicon carbide, cubic SiC (3C–SiC) and hexagonal SiC (6H–SiC) are the most common structures. Cubic SiC has a relatively narrow bandgap of 2.23 eV at room temperature and is considered to be a candidate material for high-temperature operating transistors because of its high electron mobility of up to 1000 cm²/Vs[5] and high saturation drift velocity of 2.7×10^7 cm/s at 2×10^5 V/cm.[6] On the other hand, hexagonal SiC is suitable for blue-light-emitting diodes owing to its wide bandgap of 2.93 eV.

In this study, cubic SiC films have been grown on silicon substrates by low-pressure organometallic chemical vapor deposition (LP-OMCVD). This enables the construction of devices which combine the wide-bandgap semiconductor properties of silicon carbide with the well-developed technology of silicon, such as the Si–SiC wide-gap emitter heterojunction bipolar transistor.[7] The lattice constant of cubic SiC is 4.36 Å, whereas that of Si is 5.43 Å, giving a mismatch of about −20%. Most SiC films deposited on silicon that have been used for devices are grown by atmospheric pressure CVD above 1200 °C using separate sources for silicon and carbon, such as silanes (SiH_4, Si_2H_6) or chlorosilanes (CH_3SiCl_3, etc.) and various hydrocarbons (CH_4, C_2H_2, C_2H_4, C_3H_8, etc.).[8–12] Use of silane compounds in this traditional CVD method requires safety precautions since these compounds are highly pyrophoric. Moreover this method has the disadvantage of having to maintain quite high temperatures for the deposition to occur. High temperatures for the film growth result in high tensile stress and crystalline lattice defects in the SiC film, due to the difference in lattice constants and thermal expansion coefficients (SiC 4.63×10^{-6}/K, Si 4.16×10^{-6}/K, averaged between room temperature and 1380 °C).[13] Such defects and strain in heteroepitaxial films degrade the carrier mobilities and increase junction leakage currents. Significantly lower growth temperatures are thus highly desirable. In addition to this temperature problem, manufacture of SiC device structures by CVD requires precise control of the silicon-to-carbon ratio. The use of separate sources for silicon and carbon for the growth of SiC thin films may also result in small deviations from stoichiometry in the films, leading to point defects or inclusions and precipitates. Therefore it is desirable to employ sources that are not pyrophoric

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and contain both silicon and carbon atoms. Single sources offer the advantage of using less-complicated CVD systems and, in many cases, of working at low deposition temperatures.

Low-temperature CVD of SiC on silicon and other substrates has been reported in a few cases using silacyclobutane, *c*-$C_3H_6SiH_2$,[14] 1,3-disilacyclobutane, $C_2H_8Si_2$,[15,16] methylsilane, CH_3SiH_3,[17] tetramethylsilane, $(CH_3)_4Si$,[18] diethylsilane, $(C_2H_5)_2SiH_2$,[18] tripropylsilane, $(C_3H_7)_3SiH$,[18] and hexamethyldisilane, $(CH_3)_6Si_2$.[19] In principle, the use of these single precursors offer the opportunity for improved control of the stoichiometry as well as lowering of deposition temperatures.[20]

In the present study, the growth of cubic SiC films on the Si(100) and Si(111) substrates has been carried out at a very low temperature range of 650–900 °C using a new single molecular precursor 1,3-disilabutane, [$H_3SiCH_2SiH_2CH_3$, FW 90.273, bp 39–40 °C, *d* ca. 0.674 g/mL]. The 1,3-disilabutane was selected as the precursor because it is nontoxic and nonpyrophoric, shows good pyrolysis behavior in obtaining powders of β-SiC,[21] and is readily vaporized under reduced pressure at room temperature. The molecule is also the most convenient to use among the family of the straight chain silaalkanes that have alternating silicon and carbon atoms.[23]

Experimental Section

Synthesis of the Precursor. The precursor 1,3-disilabutane which contains both silicon and carbon atoms with a Si:C ratio of 1:1 was obtained by reduction of 1,1,3,3-tetrachloro-1,3-disilabutane. The synthesis of 1,1,3,3-tetrachloro-1,3-disilabutane was reported previously by Jung[22] as follows. The reaction of (chloromethyl)methyldichlorosilane with elemental silicon and hydrogen chloride using copper as a catalyst and cadium as a cocatalyst leads to the attachment of a silicon atom to the organochlorosilane molecule, producing 1,1,3,3-tetrachloro-1,3-disilabutane. Reduction of this compound with metal hydrides (e.g., lithium aluminum hydride) in ether replaces the chlorine atoms with hydrogen atoms. The final compound is 1,3-disilabutane.[21]

Chemical Vapor Deposition. The (100) and (111) surfaces of p-type Si substrates were degreased in an ultrasonic cleaner, just prior to deposition, with trichloroethylene, followed by rinsing with acetone, deionized water, and methanol and dipping in a 20% HF solution to remove the surface oxide layer. Using a simple CVD apparatus shown in Figure 1, the precursor 1,3-disilabutane was employed to deposit SiC on Si(100) and Si(111) substrates. The CVD system (Figure 1) was built by appropriately connecting Pyrex and quartz tubings and comprised a bubbler, a deposition chamber, a liquid nitrogen trap, and vacuum pumps as major parts. The deposition temperatures were adjusted to the desired value in the range 650–900 °C and 1,3-disilabutane was then admitted into the deposition chamber. The temperatures of the substrates and/or the films were measured by an optical pyrometer. The deposition pressures, measured by a Convectron gauge during deposition, were adjusted between 25 and 55 Pa (190 and 410 mTorr), and the deposition usually lasted 4–6 h.

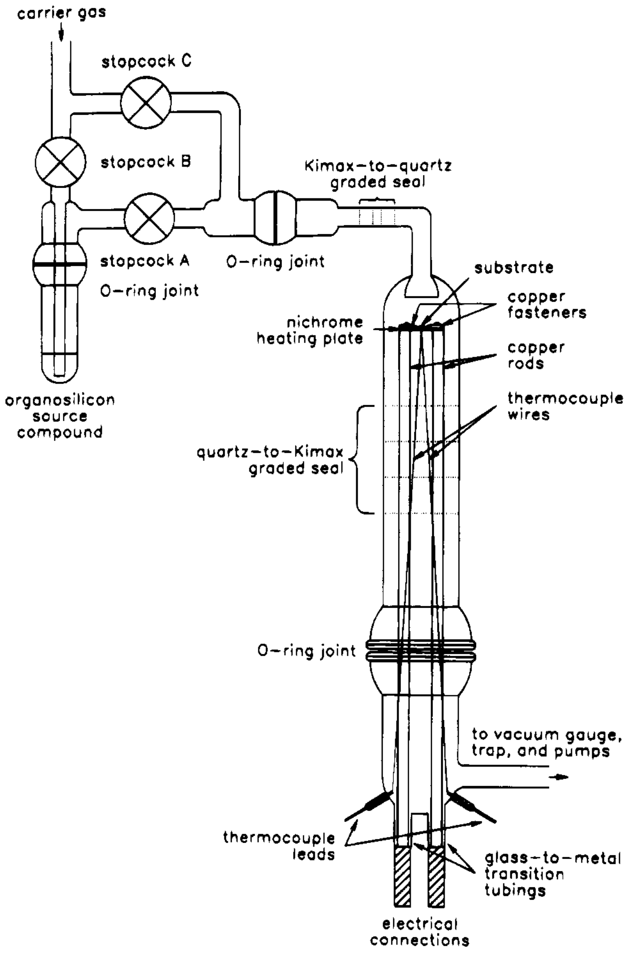

Figure 1. Schematic diagram of the LP-OMCVD apparatus.

Characterization of the Films. The films produced by CVD were characterized by X-ray photoelectron spectroscopy (XPS), X-ray diffractometry (XRD), and scanning electron microscopy (SEM), and the film thickness and growth rate were measured from SEM cross sections of the films. For XPS work, the Al K$\alpha_{1,2}$ X-ray (1486.6 eV) was used.

Results and Discussion

CVD on Si(100) Substrates. The CVD on Si(100) substrates was carried out at 650 °C. Figure 2 shows the X-ray photoelectron survey spectrum of the film deposited. The survey spectrum clearly shows the photoelectron peaks of Si 2s, Si 2p, and C 1s and C(KVV) Auger signals indicating formation of a silicon carbide film. Besides these relevant peaks, there also appear O 1s photoelectron peak and O(KVV) Auger peaks that were attributed to surface contamination of the newly formed film by air and/or moisture during sample transfer. In Figure 3, the C 1s high-resolution spectrum of this film (Figure 3a) is compared to that of a piece of bulk β-SiC (cubic SiC, Figure 3b). The bulk cubic SiC shows two types of carbon. The lower binding energy peak at 282.1 eV is attributed to carbidic carbon, and the higher binding energy peak at 284.6 eV, to graphitic carbon. The graphitic carbon comes from the graphite which is used as a binder material. Since we did not attempt to obtain accurate binding energy values, there

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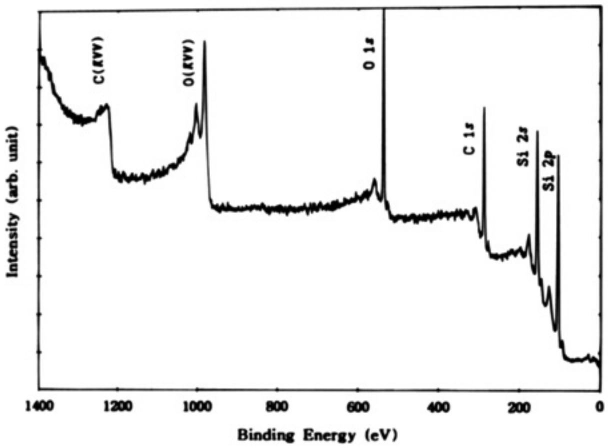

Figure 2. X-ray photoelectron survey spectrum of the film deposited on a Si(100) substrate at 650 °C.

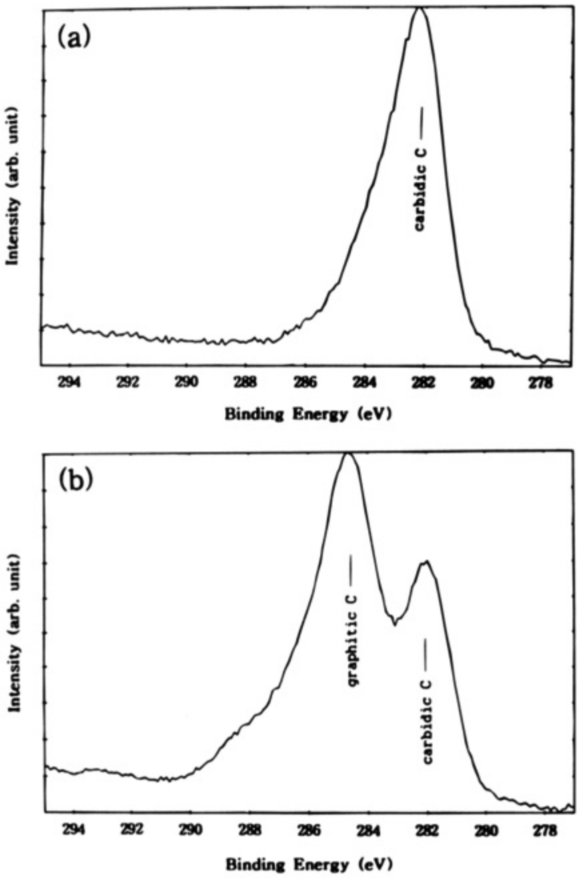

Figure 3. C 1s high-resolution spectra of (a) the film deposited on a Si(100) substrate at 650 °C and (b) the sintered body of β-SiC containing graphite.

may be some errors in the binding energy values; however, this doe not jeopardize the analysis of the X-ray photoelectron spectra. From the analysis of the C 1s high-resolution spectra of the as-grown film, we confirmed that the C 1s binding energy (282.3 eV) of our film closely matches that of the carbidic carbon of the bulk β-SiC. Moreover the peak areas of Si 2p and C 1s strongly suggest that the film has a correct stoichiomeric ratio of silicon to carbon.

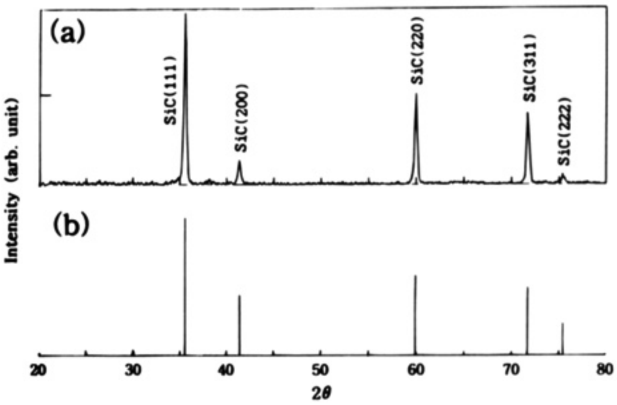

Figure 4. X-ray diffraction patterns of (a) the film deposited on a Si(100) substrate at 650 °C and (b) the β-SiC powders.

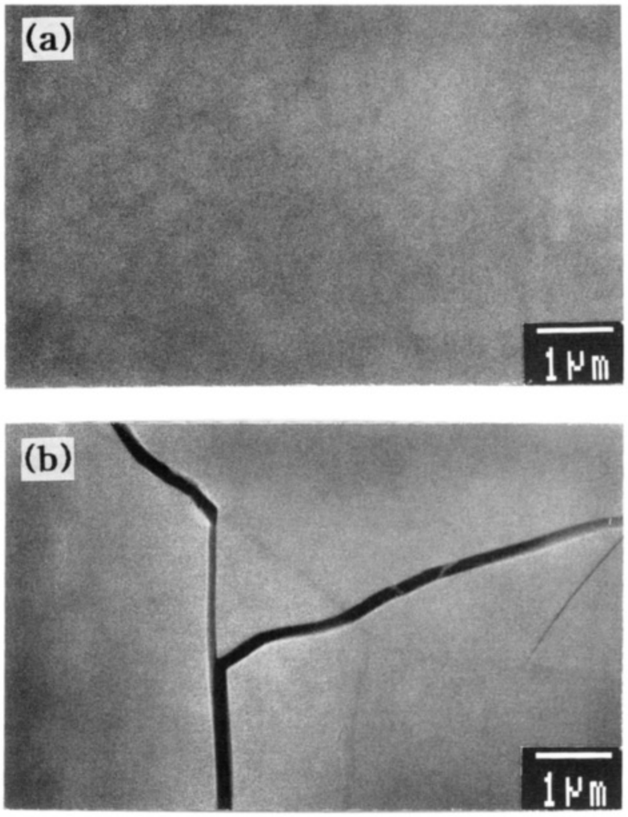

Figure 5. SEM images of the SiC film deposited on a Si(100) substrate at 650 °C: (a) smooth surface and (b) surface with cracks.

Figure 4 shows the X-ray diffraction pattern of this silicon carbide film together with the standard powder pattern of β-SiC (cubic phase) for comparison. The XRD pattern clearly indicates that the film consists of cubic SiC because the characteristic peaks due to cubic SiC appear at $2\theta = 35.6°$, 41.5°, 60°, 72°, and 75.5° that are ascribed to SiC(111), SiC(200), SiC(220), SiC(311), and SiC(222), respectively. There is no other detectable phase in the diffraction pattern. This result confirms that a cubic SiC film can be formed on a Si(100) surface from 1,3-disilabutane at such a low temperature as 650 °C. Due to the formation of a thick film, however, the substrate peaks do not show up here. The surface morphology of the film was then examined by scanning electron microscopy. Figure 5a shows a smooth surface of cubic silicon carbide with no clear shape, but a highly magnified image shows that the smooth surface actually consists of very fine grains. The peripheries of the film had an appreciable number of cracks (Figure 5b). These cracks seem to have formed partly due to the large lattice mismatch between silicon carbide and silicon and partly due to the temperature gradient through the length of the substrate (~2 cm). The film thickness and

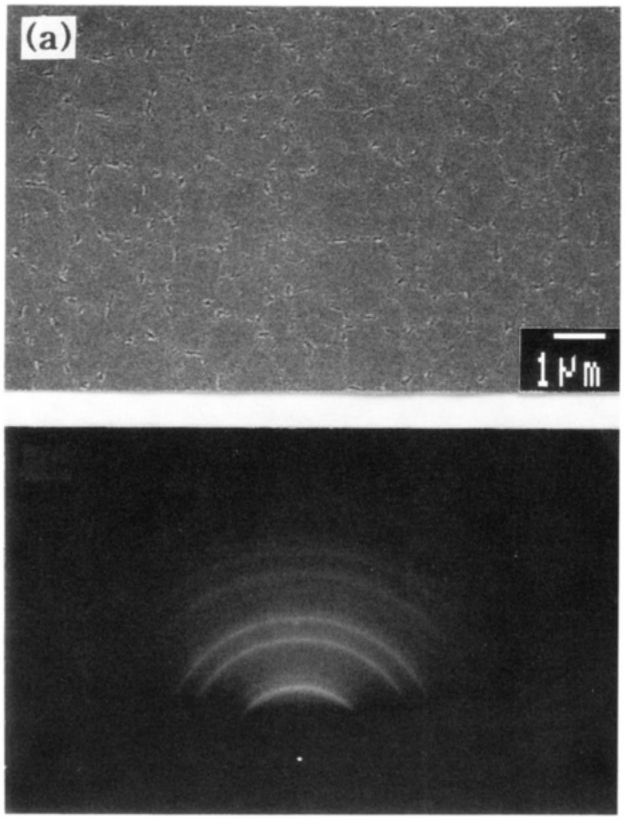

Figure 6. SEM image (a) and RHEED pattern (b) of the thin overlayer formed on a Si(100) substrate after carbonization.

growth rate were measured from the SEM cross sections. They are 6–15 μm and 1–2.5 μm/h, respectively, and they increase with deposition temperature and pressure. When the growth temperature falls below 650 °C, the XRD patterns of the SiC films formed show quite broad peaks, which implies that the SiC films are amorphous. Therefore the lowest growth temperature of cubic SiC on Si(100) substrates in our study is 650 °C.

Carbonization of Silicon Substrates. As mentioned above, the silicon carbide films formed on Si(100) substrates show quite a polycrystalline nature. In conventional CVD processes, a thin epitaxial layer of silicon carbide has to be made prior to genuine deposition to achieve epitaxial growth. In this study, this process was applied to ensure better deposition. The carbonization in this work consisted of heating the substrate in flowing methane (or propane) diluted in hydrogen (0.1–0.5%) at 1200 °C on Si(100) and at 1100 °C on Si(111) for 10–20 min. These temperatures are rather low compared to the usual practice of carbonization, but due to our limited heating capability, higher temperatures could not be obtained. Figure 6a shows the SEM image of the surface of a carbonized Si(100) substrate. In this figure, the carbonized layer is seen to consist of many small island-like regions of about 1 μm size, indicating that the carbonization is not uniform throughout the surface of the substrate. Figure 6b shows the RHEED pattern of it having ring patterns instead of spot patterns. This result shows that a thin SiC overlayer was indeed formed, but it was obviously polycrystalline, which was also confirmed by its X-ray photoelectron spectrum and X-ray diffraction pattern. From the X-ray photoelectron spectrum, it is judged that the thickness of the carbonization layer is only a few tens of angstroms.

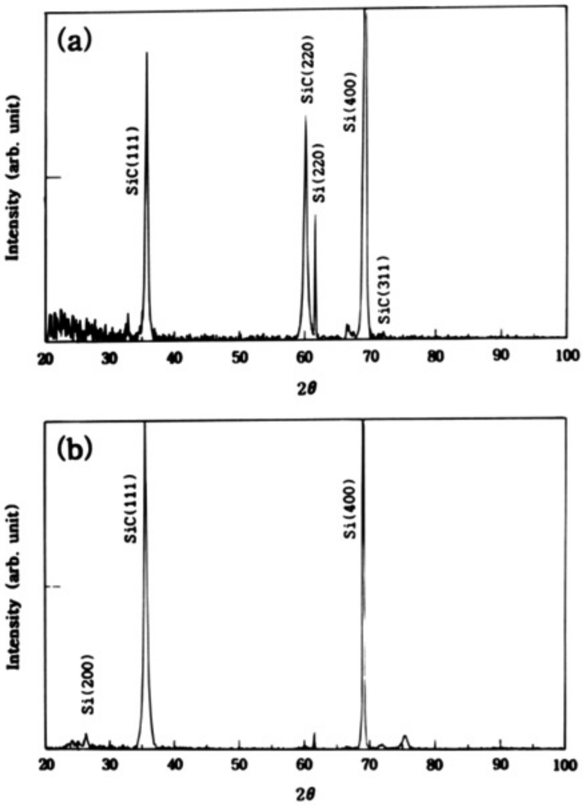

Figure 7. X-ray diffraction patterns of the cubic SiC films deposited on carbonized Si(100) substrates at (a) 850 and (b) 900 °C.

CVD on Carbonized Si(100) Substrates. The LP-OMCVD of 1,3-disilabutane was carried out at 850 °C after carbonization. The resulting film was also characterized by XPS, XRD, and SEM. Its X-ray photoelectron spectrum showed no detectable change in the binding energies of the elements nor in the individual peak shapes. Its X-ray diffraction pattern of Figure 7a, however, shows a reduced number of characteristic peaks of cubic silicon carbide. With increasing substrate temperature, this phenomenon becomes more pronounced. Figure 7b shows the X-ray diffraction pattern of a cubic SiC film deposited on a carbonized Si(100) surface at 900 °C which is characterized by a large single SiC(111) peak appearing at $2\theta = 35.6°$. The small peak at $2\theta = 75.5°$ is due to the SiC(222) diffraction. This pattern agrees very well with previous reports and is quite similar to other results.[19] In our work, the pronounced effects of carbonization of the substrate are the reduction of crack formation and the reduction of the number of SiC peaks in the XRD patterns. Judging from the RHEED patterns, we were not successful in achieving truly epitaxial growth of silicon carbide; nevertheless, this change should have some relevance to epitaxy. Further investigation is required to understand this phenomenon, and at present more precise experiments are in progress to grow epitaxial films of SiC on Si(100) substrates.

Although not shown here, the SEM images of these cubic SiC films revealed that as the deposition temperature was raised from 850 to 900 °C, the average grain size became smaller in general. It is also suggested that the adhesion of the film would be stronger after carbonization, since it was more difficult to locate the boundary between the film and the substrate in the SEM image of the cross section.

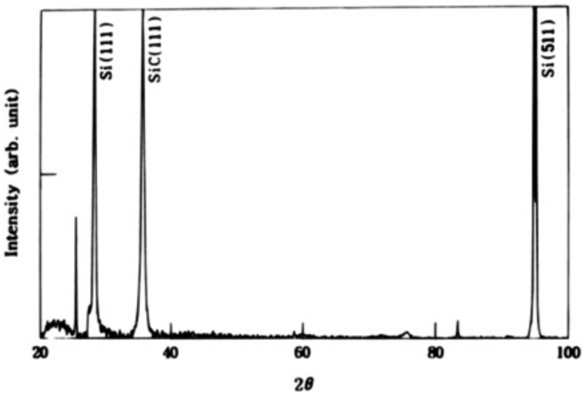

Figure 8. X-ray diffraction pattern of the cubic SiC film deposited on a carbonized Si(111) substrate at 900 °C.

CVD on Carbonized Si(111) Substrates. The LP-OMCVD of cubic SiC film was carried out at 900 °C after carbonization of a Si(111) substrate. In Figure 8, the X-ray diffraction pattern of the SiC film grown on a carbonized Si(111) substrate exhibits quite a large and sharp peak at $2\theta = 35.6°$ due to the SiC(111) diffraction. With the exception of the second-order (222) diffraction peak at $2\theta = 75.5°$, no other SiC peaks are observed. This indicates that the cubic SiC film grown at 900 °C is highly oriented in the [111] direction. This result obtained with 1,3-disilabutane at 900 °C agrees quite well with previous reports[14,19] where different precursors were employed. According to our study, the [111] direction is considered to be the preferred orientation for the growth of cubic SiC films under our growth conditions. The XRD pattern of the cubic SiC film on a carbonized Si(100) substrate also revealed that the film is strongly [111]-oriented, as shown in Figure 7.

Figure 9a shows the surface morphology of the cubic SiC film grown on a carbonized Si(111) substrate at 900 °C. It can be seen that the surface again consists of minute grains of silicon carbide. Figure 9b is the SEM cross section of the film, which shows that a thick layer of cubic SiC can be continuously grown using 1,3-disilabutane under the experimental conditions.

Conclusions

We have grown cubic SiC films on Si(100) and Si(111) substrates by low-pressure organometallic chemical vapor deposition (LP-OMCVD) between 650 and 900 °C using 1,3-disilabutane, $H_3SiCH_2SiH_2CH_3$, as a single molecular precursor.

Polycrystalline cubic SiC films were obtained on carbonized Si(100) substrates in this temperature range. According to the XRD patterns the crystallinity is improved as the deposition temperature is increased. On both Si(100) and Si(111) substrates, the preferred orientation of the film growth seems to be in the [111] direction.

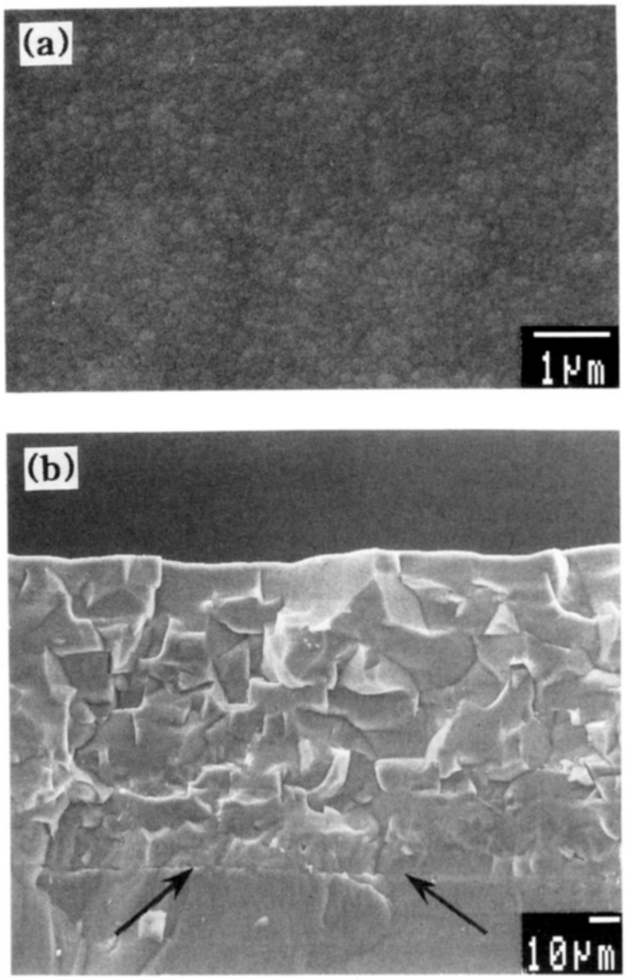

Figure 9. SEM images of the cubic SiC film deposited on a carbonized Si(111) substrate at 900 °C: (a) plan view and (b) cross section. The arrows indicate the interface.

The growth temperatures in this study are very much lower than those in previous reports. This proves that the molecular precursor 1,3-disilabutane is a promising candidate for the growth of cubic SiC on silicon substrates.

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