Growth of crystalline 3C-SiC on Si at reduced temperatures by chemical vapor deposition from silacyclobutane

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Low-pressure chemical vapor deposition of SiC on carbonized Si from the single-source organosilane precursor silacyclobutane (c-$C_3H_6SiH_2$,SCB) has been investigated from 800 to 1200 °C. On atmospheric pressure-carbonized (100)Si, SiC films grown at 900 °C and above exhibit a transmission electron diffraction pattern consisting only of sharp spots with cubic symmetry. X-ray diffraction (XRD) of these films exhibit primarily the (200) and (400) SiC lines. XRD of films grown at 900 °C on Si(111) exhibits only an extremely large SiC(111) peak with a full width at half-maximum of 450 arcsec. Using a SCB flow rate of 1 sccm, a SiC growth rate of 4–5 μm/h was obtained on Si at 900 °C. Crystalline SiC films have also been grown by SCB at a temperature of 800 °C.

The progress of SiC/Si heterojunction devices has been impeded by, among other reasons (cf. defects), the absence of a growth process which can provide monocrystalline SiC films with reasonable growth rate at temperatures low enough such as not to affect the properties of the underlying Si substrate. Most previously reported deposition of crystalline SiC on Si has utilized chemical vapor deposition (CVD) with separate C- and Si- bearing precursors, normally requiring temperatures[1–4] of 1200 to 1350 °C, with occasional lower growth temperatures (down to 1000 °C) being reported.[5,6] The C-bearing precursor is typically a simple hydrocarbon, such as propane. The Si-bearing gas is either a silane or chlorosilane gas, which are both highly toxic and pyrophoric.

This situation has spurred the investigation of alternative precursors for SiC deposition. In general, a precursor designed for this purpose[7] would contain directly bonded Si and C atoms and would decompose at relatively low temperatures into a film of stoichiometric SiC. Examples of such alkylsilane precursors reported to date include methylsilane[8,9] (CH_3SiH_3), methyltrichlorosilane[10] (CH_3SiCl_3, MTS), tetramethylsilane[11] ($\{CH_3\}_4Si$, TMS), diethylsilane[11] ($\{C_2H_5\}_2SiH_2$, DES), tripropylsilane[11] ($\{C_3H_7\}_3SiH$, TPS), hexamethyldisilane[12] ($\{CH_3\}_6Si_2$, HMDS), dimethyldichlorosilane[13] ($\{CH_3\}_2SiCl_2$, DMDS). SiC growth using TMS, DES, and TPS resulted in single crystal layer[11] on Si (111) only up to a thickness of 2000 Å. Highly oriented SiC layers were obtained[13] with DMDS at 1365 °C on both Si(100) and (111) substrates. Monocrystalline films were reported[10] for growth with MTS, but only at a temperature of 1300 °C. Use of CH_3SiH_3 for SiC growth has been reported to produce both monocrystalline layers[8] at 750 °C and amorphous layers[9] over the 650–1050 °C range. Monocrystalline SiC growth at 1000 °C has been reported[12] with HMDS.

Recently, a new class of single-source organosilane SiC precursor with a cyclic structure has been investigated: mono- and di-silacyclobutanes. Silacyclobutane (c-$C_3H_6SiH_2$,SCB) is a cyclic molecule containing one Si atom bonded to two C atoms in a four-member ring structure. SCB has been utilized for the deposition of amorphous SiC films on Si at 250 °C by plasma-enhanced CVD[14] and at 650 to 1050 °C by CVD.[9] Di-SCB has been shown[15,16] to produce predominantly 3C-SiC coatings on Si at temperatures greater than 900 °C. The SCB ring structure contains significant strain energy, thereby reducing the decomposition temperature relative to the alkylsilanes. Given the additional advantages of such a precursor, including the simplicity of a single source gas and the decreased operational hazards compared to silane, the possibility of depositing monocrystalline SiC films on Si has been investigated.

The deposition experiments were carried out in a rapid thermal CVD system equipped with a quartz chamber and IR lamps. The system has been successfully used[17,18] to grow monocrystalline SiC-on-Si films at high temperature (1100–1350 °C). SCB is a liquid at room temperature (boiling point $\approx$42 °C) with a vapor pressure of approximately 400 Torr, which enables its use without the need for a bubbler. The synthesis of SCB has been described in the literature.[19] Following synthesis, the material is distilled under Ar in a quartz apparatus and transferred to a stainless-steel container. The composition of the the distilled liquid is assessed by gas chromatography and mass spectrometry analysis at >99.5% SCB, with the balance consisting primarily of propylsilane and toluene The purity of the gas drawn from the liquid is expected to be significantly higher. SCB is not pyrophoric, but is flammable. Care must be taken to prevent condensation of the SCB in the gas delivery lines, as it can polymerize by reaction with oxygen resulting in clogging of components. When delivered with a mass flow controller, the SCB mass flow coefficient is approximately 0.2 relative to nitrogen.

The overall growth process consists of three steps. First, the Si substrate undergoes *in situ* cleaning in an HCl/H_2 atmosphere at 1200 °C. Second, a thin SiC film is

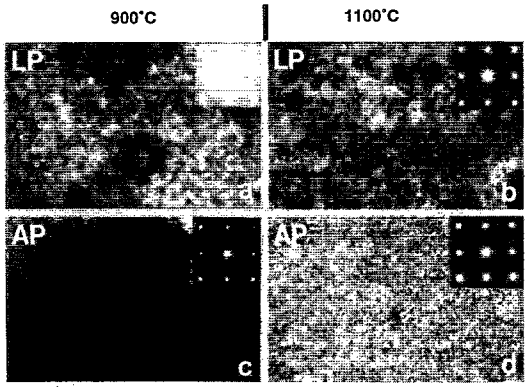

FIG. 1. TEM plan view images and TED patterns of SiC films grown on Si(100) for 1 min: (a) 900 °C SCB growth on LP carbonized Si; total SiC thickness ≈3250 Å, carbonized SiC layer ≈1200 Å. (b) 1100 °C SCB growth on LP carbonized Si; total SiC thickness ≈1800 Å, carbonized SiC layer ≈1200 Å. (c) 90 °C SCB growth on AP carbonized Si; total SiC thickness ≈2000 Å, carbonized SiC layer ≈250 Å. (d) 1100 °C SCB growth on AP carbonized Si; total SiC thickness ≈1500 Å, carbonized SiC layer ≈250 Å.

grown by propane (5% in H_2) carbonization at 1300 °C for 1 min under either atmospheric (AP) or low pressure (LP) conditions. For AP carbonization, a propane flow rate of 9 sccm is used together with a separate H_2 flow rate of 0.9 lpm, resulting in a 250-Å SiC layer. LP carbonization at 5 Torr uses propane and H_2 flow rates of 99 sccm and 0.9 lpm, yielding a SiC film of 1200 Å. Separate carbonization-only experiments were performed to measure the SiC film thickness and evaluate the surface morphology. The minimum thickness for obtaining a microscopically continuous and uniform SiC film[20] by LP carbonization under the conditions is ~1000 Å. Third, SiC films are grown by SCB pyrolysis at temperatures from 800 to 1200 °C on the carbonized surface. The growth reaction is performed at 5 Torr with 1 sccm SCB and 2 ℓpm H_2 flow. The reaction time for the experiments described here are 1 min for thinner films and 10 min for thicker films.

To investigate the structure of the SiC films grown by SCB, transmission electron microscopy (TEM) and diffraction (TED) were performed on the thinner layers. In Fig. 1 are shown TEM plan-view images and TED patterns of SiC films grown on either LP- or AP-carbonized Si(100) substrates at two temperatures (900 and 1100 °C). In general, the films grown on the AP-carbonized substrates resulted in a more uniform morphology. This is due to the rough surface produced under LP carbonization conditions. The SiC film grown at 900 °C on the LP-carbonized substrate exhibits a TED pattern [Fig. 1(a)] which indicates a combination of crystalline (periodic array of spots) and polycrystalline (ring) structures. By comparison, the film grown at the same temperature on the AP-carbonized substrate [Fig. 1(b)] indicates the presence of only crystalline material. Films grown at 1100 °C on either substrate also indicate only crystalline material.

Thicker SiC films grown on AP-carbonized Si at 900 °C yielded growth rates of ~4 and 5 μm/h for (100) and (111) substrates, respectively. For determining the growth rate, films were grown simultaneously on both

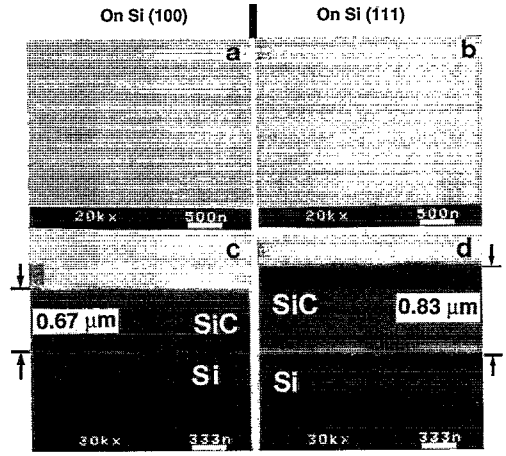

FIG. 2. SEM microphotographs of SiC films grown for 10 min at 900 °C on AP carbonization: (a) plan view on Si(100); (b) cross section on Si(100); (c) plan view on Si(111); (d) cross section on Si(111).

types of substrates. Plan-view and cross-sectional scanning electron microscopy (SEM) microphotographs of these SiC films are shown in Fig. 2. The surface morphology of both SiC films is quite smooth and the SiC/Si interface appears sharp and uniform in both cases. Conventional (θ-2θ) x-ray diffraction (XRD) spectra for these two SiC films are shown in Fig. 3. The SiC film grown on (100) Si displays major peaks for the SiC (200) reflection at 41.44° and the SiC (400) reflection at 89.9°. The full width at

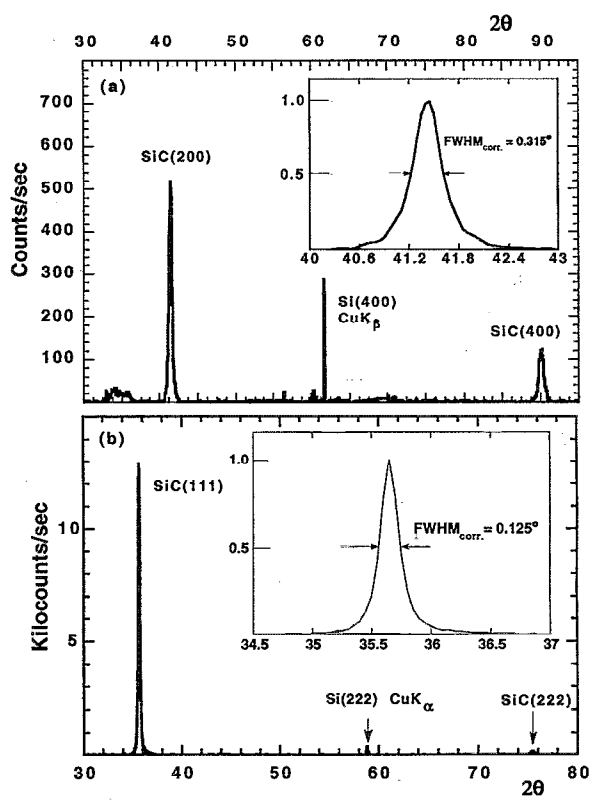

FIG. 3. XRD profiles of SiC films grown at 900 °C fro 10 min on AP carbonization: (a) 0.7 μm SiC film on Si(100); (b) 0.8 μm SiC film on Si(111).

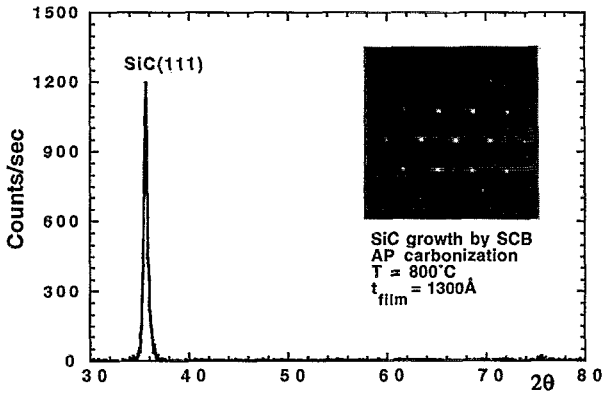

FIG. 4. XRD profile and TED pattern of SiC(111) grown at 800 °C by SCB for 1 min on AP carbonization.

half-maximum (FWHM) of the SiC (200) peak is 0.386°. If we remove the 0.08° system broadening, we obtain a corrected value of 0.315°. The XRD spectrum of the SiC film grown on Si(111) exhibits a very large and sharp peak at the (111) reflection (35.63°). With the exception of the second-order (222) reflection at 75.46°, no other SiC peaks are observed. This indicates that this SiC film grown at 900 °C is monocrystalline, with a (111) orientation. The measured FWHM of the SiC (111) peak is 0.17° and the corrected value is 0.125° or 450 arcsec. These results obtained with SCB at 900 °C compare favorably with the FWHM values reported by Nishino *et al.*[2] for SiC films grown at 1360 °C with propane on either (100) or (111) Si.

Significant further reduction of the growth temperature for SCB-grown crystalline SiC (111) is possible. For example, growth at 800 °C resulted in the crystalline x-ray and electron diffraction patterns shown in Fig. 4.

In summary, SiC thin films have been grown on Si using the cyclic organosilicon precursor SCB. Monocrystalline films have been obtained at reduced growth temperatures as low as 800 °C on carbonized Si substrates. The SiC films display an excellent surface morphology and a uniform SiC/Si interface.

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