Silicon carbide formation by annealing C_{60} films on silicon

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Silicon carbide films were grown on (100) silicon substrates by deposition of 200-nm-thick C_{60} films, followed by annealing. The predeposited C_{60} is progressively destroyed by annealing, and carbon reacts with silicon to produce SiC. The reaction starts at the interface and continues by diffusion of silicon through the already formed SiC. At the lower temperatures (700 °C), the reaction is localized at the interface. Diffusion of silicon and formation of stoichiometric SiC requires annealing at 800 °C for $t \geqslant 100$ min and at 900 °C for $t \geqslant 25$ min. The stoichiometric films are uniform with a grain size of 20–40 nm. A diffusion coefficient of silicon in SiC of 4×10^{-15} cm^2/s at 900 °C was determined. Because the diffusion of silicon is faster through preferential paths in the SiC film, such as grain boundaries and other crystalline defects, pits and voids are produced in the silicon substrate when the C_{60} predeposited film covers larger areas. © *1997 American Institute of Physics.* [S0021-8979(97)08009-2]

I. INTRODUCTION

Silicon carbide has been proposed for many years as a material for microelectronics devices with special applications and more recently for microelectromechanical (MEMS) systems applications because of its remarkable physical properties (wide band gap as a semiconductor, high thermal conductivity, chemical inertness, hardness, and wear resistance).[1–4] Different chemical vapor deposition (CVD) and molecular beam growth processes have been used for producing SiC films on SiC or Si substrates.[5–9] All these processes require a high temperature (1000–1500 °C), which restricts their application to device fabrication processes capable of withstanding such high temperature.

Recently, carbonization of C_{60} on Si was proposed as a method for producing epitaxial β-SiC on silicon at a lower temperature (800–1000 °C)[10–12] with the flexibility of patterning SiC by using the different reactivities of C_{60} toward Si and SiO_2. Our experiments focused on the growth of SiC films starting with predeposited C_{60} films on Si, examining in detail the growth process of SiC for predeposited films and the quality of the grown film.

II. EXPERIMENTAL METHODS

The substrates were (100) electronic grade 4-in. silicon wafers, degreased with organic solvents, and rinsed in deionized (DI) water. Surface contaminations were removed by RCA cleaning solution (H_2O_2:NH_4OH:H_2O, 1:1:4 at 80 °C) for 10 min, and H-terminated surfaces were produced by removing the formed oxide in a 5% HF solution ($t < 1$ min) and rinsing in DI water. The substrates were then introduced to the high vacuum (HV) chamber within a few minutes.

C_{60} films (200–300 nm thick) were deposited in a HV ($P = 10^{-7}$ Torr) chamber on the Si wafers. The wafers were extracted, cut in 1×1 cm^2 pieces, and annealed in a separate ultrahigh vacuum (UHV) chamber ($P < 10^{-8}$ Torr). To prevent loss of C_{60} by evaporation during annealing, a sandwich was formed by facing two substrates towards each other, confining C_{60} between the two plates of Si. Annealing temperatures were 700, 800, and 900 °C with times of 5, 25, 100, 150, and 300 min.

Neutral mass spectrometry by surface analysis by laser ionization (SALI) was used to measure the decomposition of C_{60} produced by annealing. The technique and instrumentation are described elsewhere.[13] Laser desorption of the material was produced by using the 355 nm line of a nanosecond Nd:YAG laser (QuantaRay), and postionization was induced by the 118 nm radiation of a picosecond Nd:YAG laser (Continuum).

The formation of SiC was detected by Auger electron spectroscopy (AES), using Si and C lineshape analysis combined with depth profiling. The AES measurements were performed using a PHI 4200 thin film analyzer. This analyzer operates at a pressure below 2×10^{-10} Torr. It has a cylindrical mirror analyzer with a coaxial electron gun. Electron beam energy and current used in the present case were 3 keV and 280 nA, respectively; the analyzer resolution was set to 0.6%. All the samples were analyzed under the same conditions. Depth profiling was performed by sputtering the sample with an Ar^+ ion gun (the 2 keV focused ion beam was rastered over a 2×2 mm area), acquiring data every 30–60 s.

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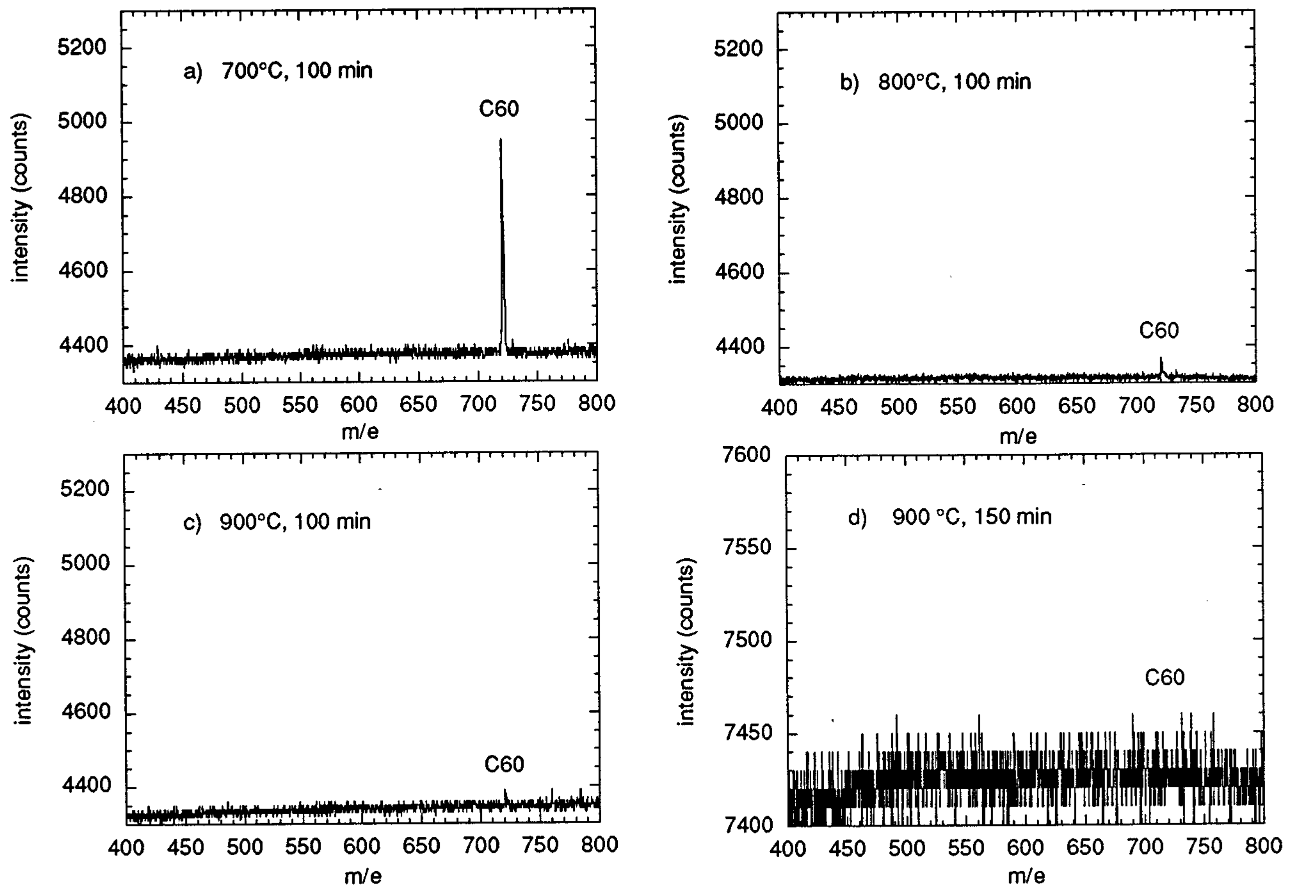

FIG. 1. SALI (surface analysis by laser ionization) mass spectra of film annealed at 700, 800, and 900 °C for 100 min: the C_{60} peak becomes progressively less intense. After annealing at 900 °C for 150 min, it completely disappears. This last spectrum was acquired for a longer time to improve the signal-to-noise ratio.

To achieve a good depth resolution in profiling and to study the formation of SiC at the interface, we performed secondary neutral mass spectrometry (SNMS)[14] depth profiling on the samples. A commercial Leybold INA 3 instrument was used with an Ar plasma. To optimize depth resolution and sensitivity in depth profiling, we chose a sputtering energy of 700 eV. The sputtering rate of SiC was evaluated by measuring, with a Dektak stylus profilometer, the depth of the crater on a sample where the depth profile had been stopped at the interface between SiC film and silicon substrate. This sputtering rate was used to convert the time scale of all the other profiles to depth, assuming that the sputtering conditions did not change between acquisitions.

The morphology of the films was investigated by scanning electron microscopy (SEM). For these measurements, the secondary electron signal was detected by a JEOL 6100 instrument, equipped with a traditional tungsten filament, operating at 25 kV. For representative samples, transmission electron microscopy (TEM) images and electron diffraction patterns were taken using a JEOL 2000FX TEM operated at 200 keV. TEM samples were prepared by chemically removing ($HF:HNO_3$:acetic acid=3:5:3) the silicon substrate. The transparent SiC films floating in the solution were collected on TEM grids.

III. RESULTS

The reaction of the C_{60} film with silicon was monitored by using SALI to measure the intensity of the C_{60} peak ($m/e=720$) at the surface of the samples. Figure 1 shows the SALI spectra of a set of samples annealed at three temperatures (700, 800, and 900 °C), for a constant time (100 min). Figure 1 also shows the spectrum of a sample annealed at 900 °C for 150 min. With increasing annealing time and temperature, the C_{60} signal decreases and no trace of the pristine C_{60} is left at 900 °C for $t>100$ min. During the annealing process, the C_{60} film is progressively consumed by the reaction with silicon to produce SiC.

Figure 2 shows the Auger depth profiles for representative samples, illustrating the kinetics of the process. The intensity of the AES signals is corrected for the relative elemental sensitivity factor and normalized to the maximum of the Si signal in the substrate. Figure 2(a) is for a sample annealed for 100 min at 700 °C. In this case, no Si is observed at the surface. The same is true for the sample annealed at 800 °C for 100 min (not shown), while for profile 2(b), 150 min at 800 °C, the silicon has diffused through the C_{60} film and reacted to give SiC.

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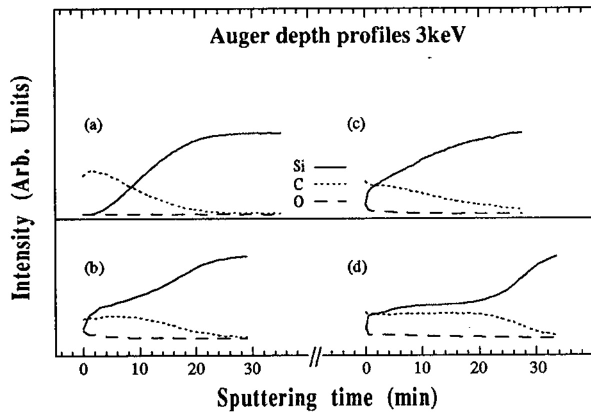

FIG. 2. Auger depth profiles for different annealing conditions: (a) 700 °C, 100 min; (b) 800 °C, 150 min; (c) 900 °C, 5 min; (d) 900 °C, 150 min.

Figure 2(c) shows the profile for a sample annealed at 900 °C for 5 min. Here the Si signal is present at the surface, but analysis of the Si and C lineshapes indicates that no reaction has taken place. However, at the same annealing temperature, but for a longer annealing time (150 min) shown in Fig. 2(d), the reaction has occurred (see below). The same is true for the sample annealed at 900 °C for 25 min (not shown). These data clearly show that the formation of SiC is controlled by Si diffusion which in turn depends on the combined effect of annealing temperature and time.

The actual formation of SiC was detected in AES by following the evolution of the C and Si AES lineshapes from graphitic carbon and elemental silicon to the typical carbide shape. The formation of SiC starts at 800 °C for anneal times longer than 100 min, while at 900 °C the reaction begins at anneal times of 25 min. At 900 °C for $t \geqslant 25$ min, the film is stoichiometric SiC, as shown by the quantitative AES depth profiles in Fig. 2.

Figure 3 shows Si *LVV* and C *KLL* derivative spectra for two samples annealed at 900 °C for 5 and 150 min, respectively. For comparison, the lineshapes in bulk and epitaxially grown SiC are also reported. The signal intensities were normalized to their respective peak-to-peak heights. In Fig. 3(b), the variation of the lineshape from graphitic carbon (solid line, 900 °C, 5 min) to carbide (dotted line, 900 °C, 150 min) is remarkable, while the similarity of the carbide to the reference samples (dashed line, bulk, and dashed-dotted line, epitaxial SiC) is striking. The evidence of Si–C bonding is also observed in all the Si lineshapes in Fig. 3(a).

To investigate whether the carbide reaction starts at the interface, we compared the width of the interface between the silicon substrate and the as-deposited or annealed C_{60} films as measured by SNMS depth profiles. The interface, very sharp for the as-deposited film, becomes wider after annealing even at the lower temperatures (700 °C) because of the beginning of the reaction between C_{60} and silicon. The SNMS profiles also show diffusion of silicon into the carbon film, as do the Auger profiles. At 700 °C, the reaction is localized at the interface, but it proceeds into the C_{60} film with increasing temperatures and times of annealing.

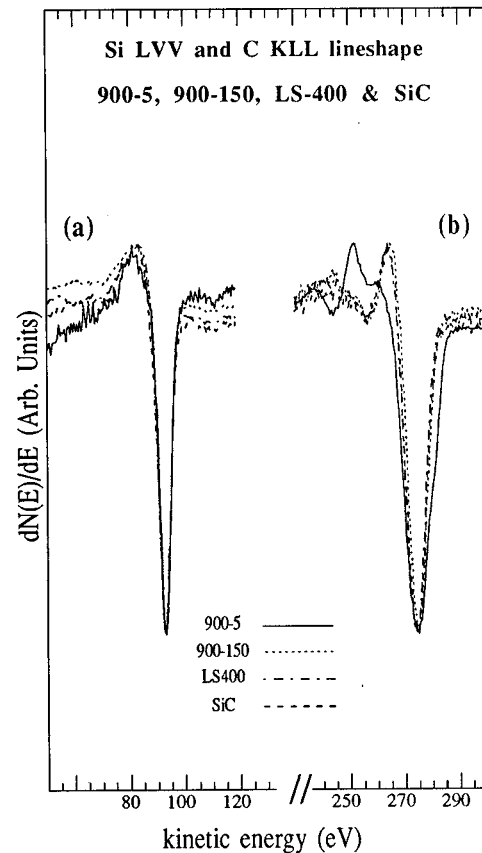

FIG. 3. A comparison of (a) Si *LVV* and (b) C *KLL* lineshapes for different samples.

For some of the samples annealed at 800 and 900 °C, it was possible to evaluate the thickness of the grown SiC layer with the SNMS method described in the experimental section. Such results are displayed in Fig. 4 as a function of annealing time.

SEM morphological observations show that these annealing conditions produce a film generally continuous and

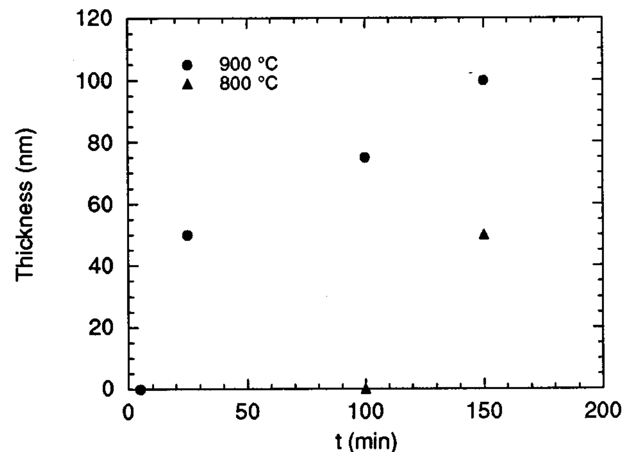

FIG. 4. Thickness of the SiC layer (as evaluated by SNMS depth profiling) as a function of annealing times at 900 °C (square) and 800 °C (triangle).

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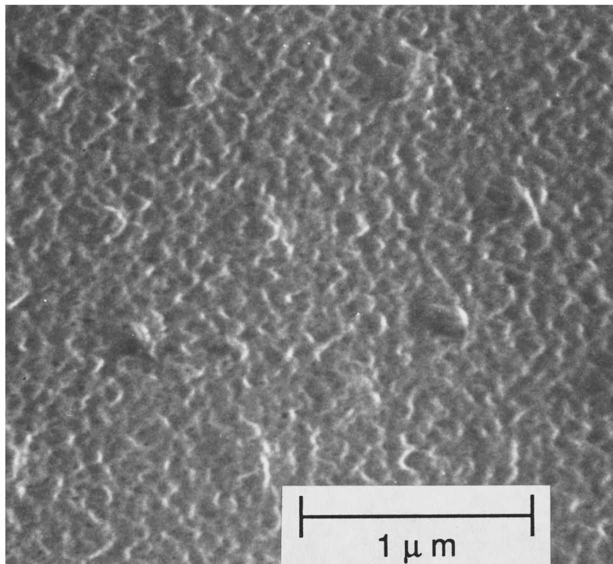

FIG. 5. SEM images of a SiC film produced by annealing at 900 °C for 150 min. Defects are present: voids in the film corresponding to pits on the substrate and hillocks corresponding to areas of enhanced growth rate due to an increased Si supply (e.g., grain boundaries).

uniform (Fig. 5, 900 °C, 150 min) with some growth defects (voids and hillocks) corresponding to enhanced diffusion paths of Si in the growing SiC film.[6,7] In films grown at lower temperatures and/or shorter times, lateral and depth uniformity, as probed by AES depth profiling, is not as good, and areas of porous SiC[7] are formed (not shown). We related these areas to the presence on the Si surface of zones of residual native oxide, detected by secondary-ion-mass-spectroscopy (SIMS) mapping. These oxide zones hinder the nucleation of SiC on the surface and promote the lateral growth of nearby SiC grains over the vertical growth of the surface nucleated grains.

TEM was used to measure the grain size and the crystallinity of the films. The Si–C material removed from the substrate by etching the samples annealed at 800 °C for 100 and 150 min and at 900 °C for 100 min consisted of a black clothlike material. Figure 6 shows the TEM image of a sample annealed at 800 °C for 100 min. The film is partially converted carbon and amorphous SiC. In contrast, the sample, annealed at 900 °C for 150 min, produced a very transparent self-standing large film produced by removing the substrate.

Figure 7 shows the TEM image of this sample. The grain size ranges between 20 and 40 nm. Some unconverted carbon is still present in the grain bulk, giving a darker color to some of the grains. Also, crystallographic defects (twins, dislocations) are evident in some grains. The lattice parameter given by the analysis of the electron diffraction pattern is characteristic of SiC, but it is not possible to discriminate between the α-(hexagonal) and β-(cubic) SiC types.

IV. DISCUSSION

Although the reaction of C_{60} molecules with (100) and (111) silicon surfaces has been previously demonstrated,[10–13] our findings suggest an alternative path for growing SiC films on silicon by starting with predeposited films. In this approach, the problem to overcome is that of confining the C_{60} on the surface at a temperature high enough ($T>800$ °C) to allow the reaction with Si to proceed (C_{60} multilayers desorb at about 350 °C). Our method of facing two substrates allows the buildup of sufficient C_{60} overpressure during annealing to confine most of the predeposited C_{60}. At the edges of the ''sandwich,'' part of the film evaporates off, but at this stage we do not consider the lateral uniformity on the entire sample area to be the main issue.

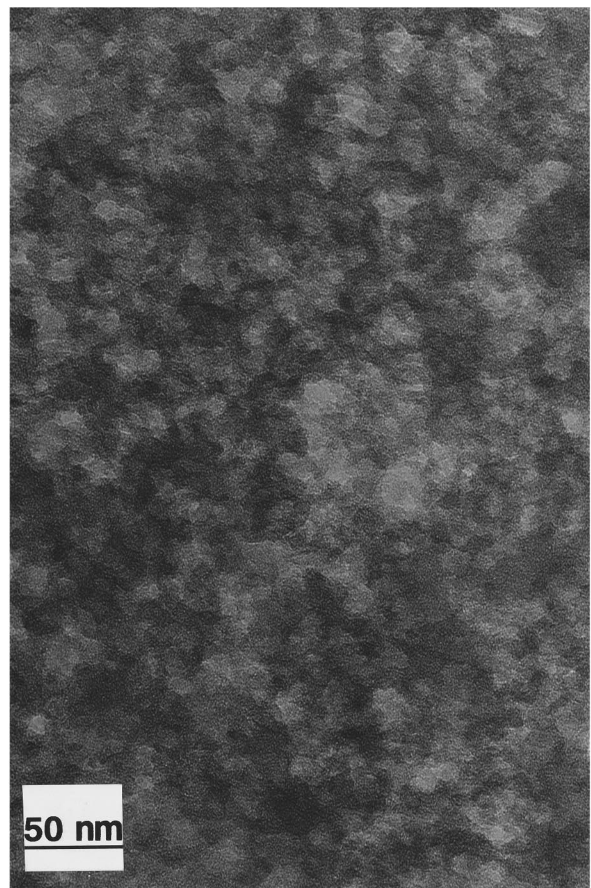

FIG. 6. TEM image ($E=200$ keV, magnification=150 000) of a film annealed at 800 °C for 100 min, showing areas of partially reacted carbon and amorphous SiC.

Alternative methods of confining C_{60} by depositing capping layers for the annealing can be implemented. Among these, the use of an ''ion modified'' C_{60} capping layer was presented by our group in a previous paper.[15] Confining C_{60} in selected areas with a capping layer may be a way of patterning SiC structures on silicon more directly and faster than the method suggested by Hamza *et al.*[10,11] based on the different reactivity of a C_{60} beam on silicon and SiO_2 surfaces.

The diffuse interface between the predeposited C_{60} film and the substrate shown by our depth profiles of samples annealed above 700 °C confirms that the reaction of C_{60} with Si starts at the interface between the C_{60} layer and the Si substrate. In the same range of temperatures, Hamza *et al.*[10] reported the formation of silicon carbide on Si (100) for continuous exposure of the surface to a C_{60} flux. Nucleation of

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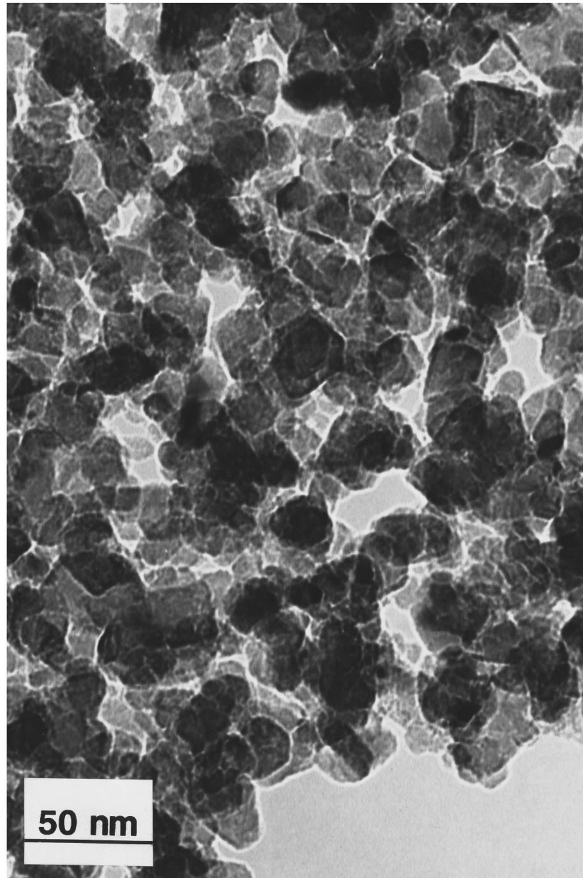

FIG. 7. TEM image ($E = 200$ keV, magnification = 150 000) of a film annealed at 900 °C for 150 min. Note the presence in some grains of unreacted carbon and of bulk grain defects (twins and dislocations).

SiC grains, which eventually coalesce to form a continuous polycrystalline film, is very fast in the early stage of annealing and is made possible by the large quantity of carbon already present (Fig. 2).

The high density of nucleation sites is also suggested by the smaller grain size (20–40 nm) and the higher density of intergrain defects (i.e., twins and dislocations) seen by TEM in SiC film produced by predeposited C_{60} compared with the crystallite size (100 nm) and quality measured in a sample produced by molecular beam, following the process of Hamza and co-workers.[10–12]

The growth of the SiC layer proceeds more slowly (Fig. 2) after this initial nucleation stage. For the annealing times and temperatures investigated in our work, the formation of a significant thickness of SiC occurs for $t > 100$ min at $T = 800\ ^\circ C$ and for $t > 25$ min at 900 °C.

It had been pointed out earlier, in Refs. 6–8 for the carbonization reaction of hydrocarbons on silicon and in Refs. 10 and 11 for C_{60} impinging on silicon surfaces, that the limiting factor for the growth of SiC films is the diffusion of silicon into the C_{60} film through the already formed SiC layer. Figure 8, which plots the SiC thickness as function of $t^{1/2}$, where t is the annealing time at 900 °C, supports that explanation.

By using the data of Fig. 8, we estimate the diffusion coefficient of silicon in silicon carbide at 900 °C to be 4.8 $\times 10^{-15}$ cm^2/s. This value is consistent, within the relatively large experimental error due to the thickness evaluation and the small number of experimental points available, with the value (7.7×10^{-14} cm^2/s) that can be estimated from the work of Hamza and co-workers[10] (500 nm, 260 min) by applying the Graul–Wagner expression.[8] Furthermore, using Graul–Wagner diffusion coefficient at 1250 °C and our diffusion coefficient at 900 °C, we estimate an activation energy (E_a) of 1.17 eV for the diffusion process.

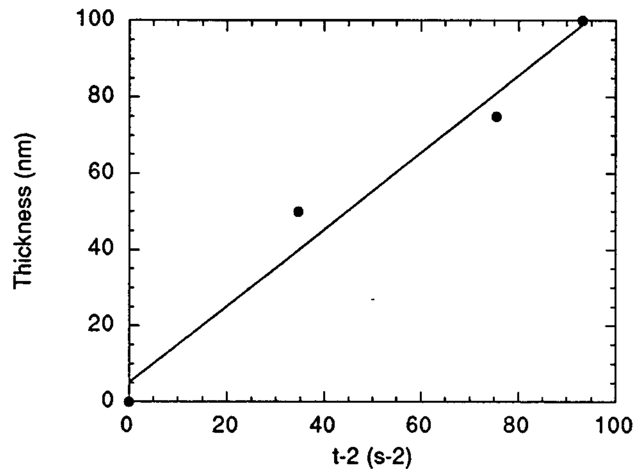

FIG. 8. Dependence of SiC layer thickness on $t^{1/2}$ with t annealing times at 900 °C.

Note that all the experimental evidence given by TEM and AES on the mechanism of formation of SiC film on silicon are in striking agreement. The interdiffusion of silicon in carbon and their incomplete reaction suggested by analysis of AES profiles and lineshapes of the samples annealed at 800–900 °C for $t < 150$ min is demonstrated in TEM photos by the presence of unreacted carbon and amorphous SiC. In contrast, the stoichiometric film is more transparent because its larger size grains have a better crystallographic quality (fewer twins and dislocations and no unreacted carbon).

When the C_{60} predeposited film covers larger areas as in these samples,[16] the Si necessary for the reaction diffuses through the already formed SiC layer preferentially at defect sites in the films (e.g., grain boundaries). Further support to this hypothesis is given by the residual zones of unreacted carbon seen by TEM in the central areas of the grains for samples annealed at lower temperature and shorter times. In the silicon substrate, these preferential diffusion paths lead to formation of the voids in the silicon substrate observed by SEM. Similar voids on the silicon substrate were reported by Cheng *et al.*[11] for C_{60} molecular beam formation of SiC and by Li and Steckl[6] and Mogab and Leamy[7] for CVD deposition.

V. CONCLUSIONS

Our experiments have proved that homogenous SiC films on silicon substrates can be produced from predeposited C_{60} films on silicon by annealing at 900 °C. When the C_{60} predeposited film covers larger areas, the Si necessary

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for the reaction diffuses through the already formed SiC layer preferentially at defect sites in the films (e.g., grain boundaries). In the silicon substrate, these preferential diffusion paths lead to pit formation. Further investigations are in progress to evaluate the mechanical and electrical properties of the SiC films.

ACKNOWLEDGMENTS

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[16] When smaller structures are patterned on a silicon surface, surface diffusion of Si becomes the predominant mechanism (see Ref. 15).

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