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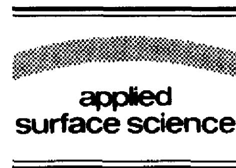
Applied Surface Science 119 (1997) 76–82



Growth of patterned SiC by ion modification and annealing of C_{60} films on silicon

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Received 11 September 1996; accepted 16 November 1996

Abstract

Silicon carbide films on silicon have been grown by annealing of pre-deposited C_{60} film on silicon at $T = 900°C$ for 300 min. C_{60} molecules are confined on the surface during annealing by a non-volatile carbon layer produced by irradiation of the C_{60} film with an ion gun (Ar^+ or Ga^+). During annealing the C_{60} film confined in the irradiated areas forms SiC while the remaining C_{60} evaporates off. These results introduce a new method of direct patterning SiC structures on Si with submicron resolution. © 1997 Elsevier Science B.V.

1. Introduction

Silicon carbide has been proposed for many years as a material for microelectronics devices with special applications (high temperature, high power, high frequency) ([1] and references cited) and more recently for MEMC (microelectromechanical systems) applications [2–4]. Among the physical characteristics which make this material particularly attractive are its wide band gap, which allows the material to be used as a high temperature semiconductor, its high thermal conductivity and its chemical inertness, hardness and wear resistance. Production of high quality crystalline SiC films has proved difficult but in addition its low chemical reactivity with liquids and gases makes the etching processes necessary for the fabrication of devices difficult and limits its use in commercial devices.

The CVD (chemical vapor deposition) growth of SiC films by carbonization of acetylene, propane or methane on silicon substrates, sometimes with an extra supply of silicon (by SiH_4 or SiH_2Cl_2 gases) has been reported [5–9]. These processes require a fairly high temperature (1000–1500°C). For example, Zorman et al. [4] reported successful CVD growth, at 1400°C, of single crystal 3C-SiC films on 4″ Si(100) wafers.

Recently carbonization of Si by C_{60} has been

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PII S0169-4332(96)01086-0

proposed as a method to produce epitaxial β-SiC on silicon at lower temperatures (800–1000°C) [10]. Because C_{60} does not react with SiO_2 surfaces, the use of patterned Si/SiO_2 substrate has been suggested for selective growth of patterned SiC on Si. This approach has been followed by a few groups and the process for growing SiC has been described [11,12]. In all of these cases a beam of C_{60} impinged on the surface of a silicon substrate held at temperature of 800–1000°C.

In this paper we report a different approach which allows direct ion beam patterning of SiC structures on silicon substrates starting with a pre-deposited C_{60} film. Similar patterning of thin film by ion beam modification has been reported for SAM (self assembled monolayer) films [13] and ion beam assisted chemical reaction have been used to produce patterned oxides and nitrides layers for microelectronics [14]. In our work, the fabrication of submicron SiC structures on silicon starting with C_{60} layers is demonstrated in a very simple process.

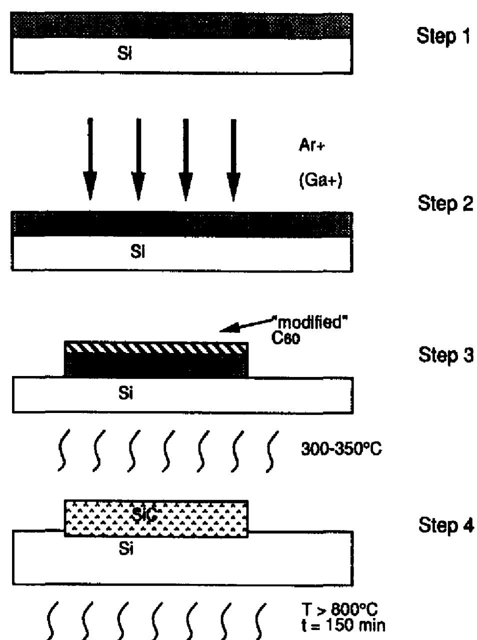

Fig. 1. Process layout: step (1) deposit C_{60} on Si; step (2) irradiate selected areas with Ar^+ (Ga^+); step (3) heat to 350°C, C_{60} evaporates from areas not irradiated with Ar^+ (Ga^+); step (4) heat to ≈ 850°C, reaction between Si and C_{60} gives SiC.

2. Process layout

Silicon substrates (1 × 1 cm) were cut from (100) and (111) electronics grade silicon wafers. Samples were degreased using organic solvents and rinsed in de-ionized (D-I) 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 D-I water. The sample was introduced into the UHV chamber within a few minutes. Our process for the fabrication of patterned SiC on Si is shown in Fig. 1. It consists of the deposition of a 200–300 nm thick C_{60} film on a Si substrate in a UHV chamber ($P < 10^{-8}$ Torr). After deposition, the C_{60} film is surface damaged in selected areas with a rastered ion beam (Ar^+ or Ga^+ ions). The interaction of the energetic primary ions with the top layers of the C_{60} film creates a non-volatile layer which acts as a cap to confine the underlying C_{60} on the surface and permits the high temperature SiC growth. The undamaged C_{60} sublimes away but the confined layer is converted to SiC in the selected areas defined by the ion beam irradiation.

3. Results and discussion

3.1. Capping layer formation

The effectiveness of the capping layer is independent of Ar^+ ion energy, in the range of 2–7 keV. In our first set of experiments, the Ar^+ ion flux was in the range of 10^{14} ions/cm^2/s and the beam was rastered over areas of about 0.25 cm^2. No difference has been seen for irradiation doses between 10^{15} and 10^{16} ions/cm^2. That surface adsorbed oxygen did not affect the capping layer was established by comparing samples produced by in-situ and ex-situ (after exposure to air) bombardment. High spatial resolution experiments were conducted using a liquid metal Ga^+ ion gun (LMIG) at an energy of 20 and 25 keV. The ion flux was 10^{18} ions/cm^2/s and the beam was rastered over areas of 10^{-5}–10^{-3} cm^2. The irradiation doses ranged between 10^{13} and 10^{16} cm^{-2}.

Ion irradiation produces a visible change in the optical properties of C_{60} films allowing the patterns to be viewed in an optical microscope. The penetration depth of the primary ions is used to estimate the thickness of the modified layer. According to TRIM [15] simulation, 7 keV Ar^+ ions penetrate about 11 nm and 20 keV Ga^+ penetrate 21 nm or about 10–20% of the C_{60} film thickness used in these experiments. The nature of the modification induced by the ion beam on C_{60} is not well understood. In this energy range the dominant mechanism of energy loss is by nuclear collisions (for 7 keV Ar^+ $(dE/dx)_{nuc}/(dE/dx)_{el} = 3.6$) which break up the C_{60} cages and permit them to cross-link into a graphite-like or amorphous carbon layer. Preliminary Raman analyses of irradiated C_{60} films show a reduction of the C_{60} peak intensity in the irradiated areas. Also the Si peak decreases due to an apparent increased opacity of the carbon film as reported by Prawer et al. [16]. The same group explained the induced change in the C_{60} film by the interaction of keV Ar^+ beams in terms of the catastrophic break down of the molecular cage [17].

3.2. SiC growth

Subsequent to the ion bombardment, the film is annealed in the same UHV chamber at 900°C (ramp rate 20°C/min) for times ranging between 150 and 300 min. The ranges of annealing temperatures and times were chosen on the basis of an earlier work on the formation of SiC from pre-deposited C_{60} films [18]. As the temperature climbs through 300–400°C, the unmodified C_{60} film evaporates off. However, at

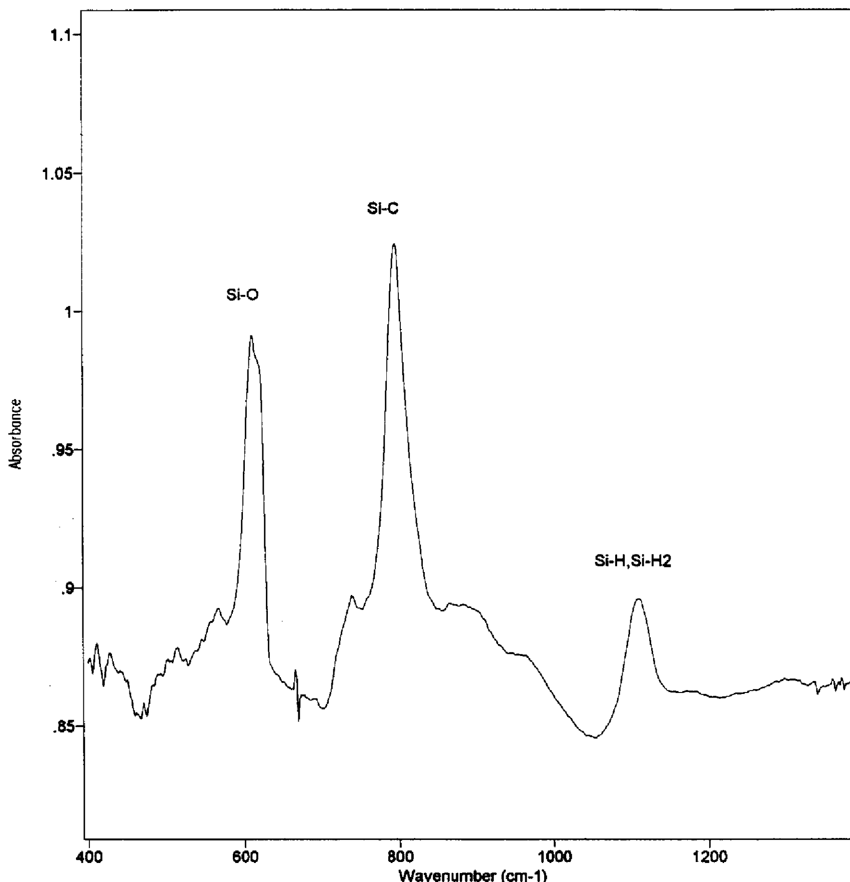

Fig. 2. Infrared spectra of the grown film showing an adsorption peak at 795 cm^{-1} typical of a SiC film. The two other peaks, assigned to Si–H and Si–O bondings, are due to a incomplete subtraction of the original substrate spectrum.

temperatures above 800°C the confined C_{60} molecules in the irradiated areas begin to react with silicon diffusing upward from the substrate to form a SiC film. Although the thickness of the capping layer is about 10% of the original C_{60} film thickness, no measurements have been made of the effectiveness of the capping layer for confining all of the deposited C_{60} at high temperatures. However from depth profile measurements we estimate that SiC films with thicknesses of at least 80 nm have been grown by this method.

Pure SiC films of area 5×5 mm^2 irradiated by Ar^+ are obtained under these conditions of film thickness and ion dose at 900°C, with annealing times of 300 min. The uniform formation of carbide and absence of free carbon was demonstrated by Auger depth profile analysis. The SiC composition was also confirmed by transmission FT-IR spectroscopy (Fig. 2) as well as by electron diffraction and HR-TEM analysis. Fig. 3a shows a TEM image of a SiC film collected on a TEM grid after etching ($HF:HNO_3$: acetic acid = 3:5:3) off the silicon substrate. The film is polycrystalline with an average grain size of 40 nm. Twins and crystallographic defects are present in the bulk of the grains. Measurement of the lattice spacing in HR-TEM images as the one shown in Fig. 3b allowed us to identify this SiC as a polytype α-SiC with no preferential orientation of growth. The growth of SiC was independent of the orientation of the Si substrate.

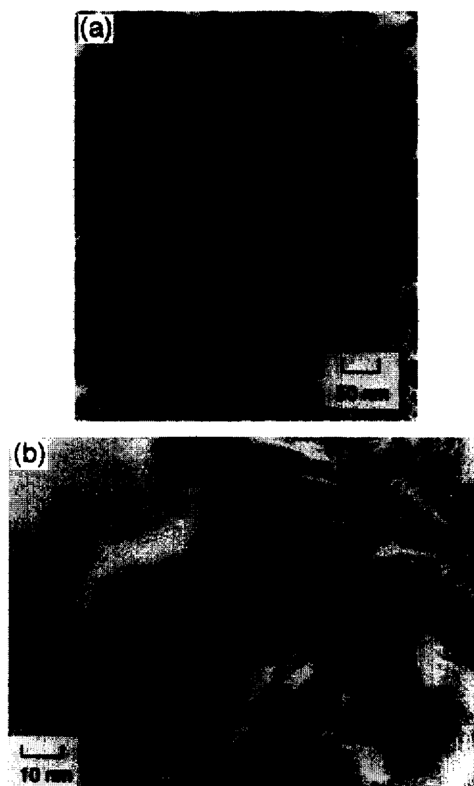

Fig. 3. TEM (a) and HR-TEM (b) images of a SiC film removed from the silicon substrate by chemical etching.

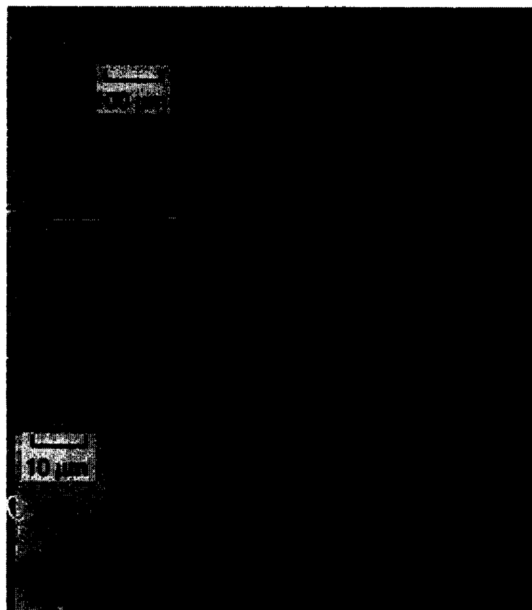

Fig. 4. Optical microscope image of strips written by a LM-ion gun. The insert is a magnification of the marked area.

The film morphologies show cracks and wrinkles due to the intrinsic stress of the growing film enhanced by the thermal stresses produced by the cool down processes (SiC and Si have 8% thermal and 20% lattice mismatches). Furthermore, in this process which starts with pre-deposited C_{60} films, we propose that film buckling is produced by the increase in volume necessary to accommodate the silicon atoms diffusing into the C_{60} film. Using the typical interatomic Si–C distance of crystalline SiC and assuming isotropic expansion in the three spatial directions, the linear expansion relative to the initial dimensions of the original C_{60} film is in the range of 20 to 60% depending on the crystallinic ordering. Buckling and interfacial decohesion in zones of

weakness of the interface (i.e. in presence of defects or cavities on the surface) permit wrinkling to relieve the built up stress [19]. In these large-area films, large pits in the silicon substrate underlying the formed film are also evident. The formation of pits in the substrate is a characteristic feature of large area SiC growth by carbonization of silicon substrates [6,7,11]. Since bulk diffusion of silicon in SiC is very slow [8,11], the silicon instead diffuses towards the unconverted carbon along surfaces or grain boundaries (or generally defects) in the already formed SiC layer. Thus very localized depleted zones can be created on the silicon substrate due to defects present on the surface.

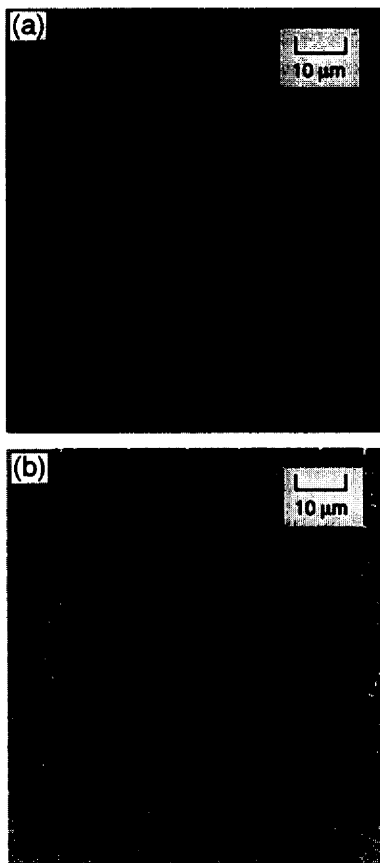

Fig. 5. Optical images of an irradiated area before (left) and after (right) annealing ($T = 900°C$, $t = 300$ min). No loss of resolution is observed at this magnification.

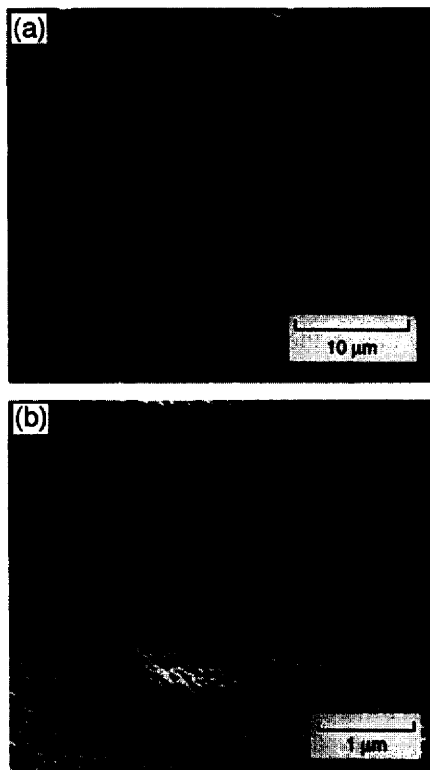

Fig. 6. SEM image of a SiC film produced by Ga^+ ion modification followed by annealing ($T = 900°C$, $t = 300$ min) showing wrinkles and ridges on the SiC film (a). At higher magnification (b) the morphology is uniform over ridges and valleys.

3.3. High resolution patterning

The success of this method of growing SiC films on Si suggested its use for producing patterned structures of SiC on Si (Fig. 4). To investigate the lateral resolution achievable on SiC structures by ion beam patterning of a C_{60} film, a high resolution LM-ion gun was used. By rastering the ion beam, a series of 3 strips (1.2 mm long and, respectively, 350, 120 and 30 μm wide) were irradiated on the C_{60} film with increasing doses (10, 20 and 30 s, corresponding to doses of 1.5×10^{15}, 3×10^{15} and 4.5×10^{15} ions/cm^2). A fourth set of 3 strips with linear dimensions reduced by a factor 3 was rastered for 10 s (dose $= 1.5 \times 10^{16}$ cm^{-2}). In Fig. 5 the optical image of the end of one strip before (a) and after (b) annealing shows almost no loss of resolution, on the micron scale, due to the annealing. The inset of Fig. 4 is an enlargement of one end of the narrowest pattern which shows a submicron wide SiC line

produced by a single trace of the ion beam as it moves between rastering positions. These SiC lines have the lateral dimension of the LMIG beam (< 1 μm).

In these small size features, cracking is not evident perhaps because the mechanical and thermal stress between SiC and silicon substrate is more easily relieved. Also, pitting of the substrate was never observed in these samples. Nevertheless SEM photos show the SiC film morphology to consist of valleys and ridges due to the volume change discussed above (Fig. 6a). Higher magnification SEM images of the wrinkled areas (Fig. 6b) show the films to be uniform in grain size and distribution over the ridges and valleys.

As can be seen in Figs. 4 and 5, the largest size SiC grains are located at the edges of the strips at the boundary between bare silicon and SiC. The growth of these edge grains is facilitated by the abundant Si available by diffusion from the bare Si surface and appears to pin the edges of the SiC to the Si. Evidently decohesion due to removal of Si from the area underlying SiC film permits the film to buckle and form ridges. The role of the ion dose on film morphology was further investigated with the LMIG gun at lower doses. Fig. 7 shows 400×100 μm strips irradiated with doses increasing from 6.7×10^{12} to 6.7×10^{13} ions/cm^2. In this case, the film

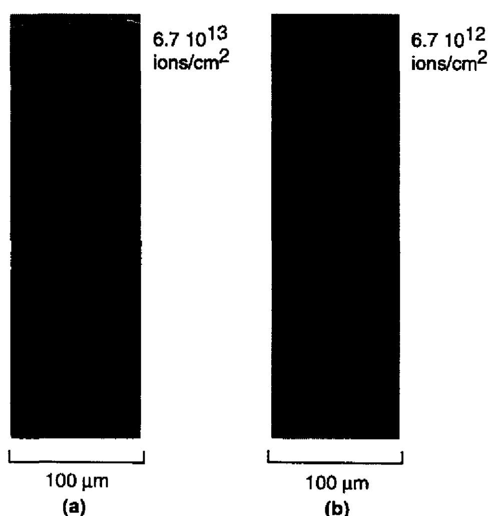

Fig. 7. SEM images of SiC strips produced by LMIG gun with increasing doses (in ions/cm^2): 6.7×10^{13} (a) and 6.7×10^{12} (b).

strips buckle mainly in the longitudinal direction (the folds are perpendicular to the strip length) and the number of wrinkles increases with dose. Optical observations of the structures before annealing have shown that individual scan lines are visible (each about 0.4 μm wide, which is the measured size of the LM-Ga beam). In these runs the ion current was kept constant and the dose was increased by increasing the number of longitudinal scans in a given area. For the lowest doses, gaps between scan lines, can be as much as 30–40% of the total strip area, decreasing for higher irradiation doses. This free surface permits Si diffusion along the edge of the individual lines and allows lateral expansion of the growing film to relieve intrinsic stress. However expansion in the longitudinal direction is still relieved by folds across the strips as is evident in Fig. 7. With increasing dose the interline gaps disappear due to overlap and the lateral tension then causes lateral as well as longitudinal, wrinkles as in Fig. 6. It is again noteworthy that SiC growth at the edges of the original C_{60} film (Figs. 4 and 5), is pinned by its rapid growth which permits the dimensions of the SiC structures to be defined by the irradiation with sub-micron precision. Therefore, since an expansion of the film as a whole is not allowed, buckling and decohesion of film occurs unless it can be relieved by interline gaps. It has been demonstrated theoretically and experimentally [19] that these are the typical modes of stress relaxation for films on substrates with weak interface (e.g. caused by interfacial cavities as for SiC).

4. Conclusions

We have shown that a thin ($\approx$ 20 nm) ion-irradiated C_{60} layer can confine C_{60} molecules on a Si surface up to 900°C. As a consequence, α-SiC polycrystalline films with an average grain size of 40 nm can be formed by annealing of pre-deposited C_{60} films on silicon after ion modification of the top layer of C_{60} by irradiation with keV energetic ions. Structures of SiC with lateral resolution defined by the ion beam size (< 1 μm for LMIG guns) can be patterned on the silicon substrate. In micron size features the formation of pits, is avoided by the

larger source of silicon atoms from surface diffusion. However, stress induced buckling and partial decohesion due to volume expansion of the SiC films is still observed. Our results suggest that sub-micron size structures formed with low ion doses (around 10^{13} ions/cm^2) obtained by discrete point irradiation that provide gaps for Si diffusion may avoid the problem. Further investigations are in progress to characterize the structural, mechanical and electrical characteristics of these silicon carbide films.

Acknowledgements

Part of this work was conducted under the program 'Advanced Chemical Processing Technology' consigned to the Advanced Processing Technology Research Association from the New Energy and Industrial Technology Development Organization, which is carried out under the Industrial Science and Technology Frontier Program administered by the Agency of Industrial Science and Technology, The Ministry of International Trade and Industry, Japan.

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