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SiC film growth on Si(111) by supersonic beams of C_{60}

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Abstract. The development of electronic devices based on Silicon Carbide (SiC) has been strongly limited by the difficulties in growing high quality crystalline bulk materials and films. We have recently elaborated a new technique for the synthesis of SiC on clean Si substrates by means of supersonic beams of C_{60}: the electronic and structural properties of the film can be controlled by monitoring the beam parameters, *i.e.* flux and particles energy and aggregation state. SiC films were grown in Ultra High Vacuum on Si(111)-7×7, at substrates temperatures of 800 °C, using two different supersonic beams of C_{60}: He and H_2 have been used as seeding gases, leading to particles energy of 5 eV and 20 eV, respectively. Surface characterisation was done *in situ* by Auger and X–Ray photoelectron spectroscopy, as well as by low energy electron diffraction and *ex situ* by atomic force microscopy technique. SiC films exhibited good structural and electronic properties, with presence of defects different from the typical triangular voids.

PACS. 68.55.Jk Structure and morphology; thickness; crystalline orientation and texture – 68.35.-p Solid surfaces and solid-solid interfaces: Structure and energetics – 68.37.Ps Atomic force microscopy (AFM)

1 Introduction

Silicon Carbide (SiC) is a wide gap semiconductor (2.2–3.3 eV) that is attracting great interest because of its extremely good properties such as thermal stability and conductivity, high breakdown voltage, high resistance to hostile environments, high hardness [1–3]. These properties make SiC ideal for use in high frequency, high power devices. This material is known to be present in several polytypes, due to the two different crystallographic structures, hexagonal (α) and cubic (β). The only cubic polytype (3C-SiC) has potentially the best electrical properties and, above all, can be grown directly on Si since it is the lowest-temperature phase. Great effort has been made to grow good quality SiC films by heteroepitaxy on silicon. Unfortunately, the great lattice (20%) and thermal (8%) mismatch [4], as well as the high reaction temperatures (above 1000 °C for standard thermal techniques, such as Chemical Vapor Deposition, CVD), lead to the growth of rough surfaces with a high density of defects [5–7]. The presence of triangular or square shape voids for such films has been reported. They are related to the diffusion mechanism of Si from the substrate to the SiC surface uppermost layer: in fact, the low diffusion coefficient of Si in SiC inhibits carbide formation when film thickness is reasonably high. The lowering of the deposition temperature should improve crystalline quality and could be achieved by a good control on the growth conditions and by using the correct type of the precursors. The use of energetic carbon atoms or carbon-based molecules with a few to tens eV can lower the epitaxial growth temperature. This results in suppression of defect formation at the interface [8]. Fullerene (C_{60}) has been demonstrated to have a strong interaction with the Si(111) surface [9], even at room temperature. It has been successfully used as a precursor for epitaxial growth, as a lower growth temperature is required and thin as well as thick film can be grown [10–12].

We have previously shown that the use of Hyperthermal Supersonic Beams (HBS) of C_{60} allows the growth of SiC thin films at lower substrate temperature than for standard methods [13]. The HBS technique [14–16] utilises a highly collimated flux of neutral particles, a supersonic beams of C_{60} whose density, particles kinetic energy and aggregation state can be varied by changing the beam parameters. In particular, the kinetic energy of the impinging fullerene cage ranges from 0.5 eV up to 100 eV, therefore well above the thermal energy of the commonly used evaporation techniques (about 0.05 eV). In such a way, the Si-C bond formation on the Si surface can be obtained by kinetic activation at a lower substrate temperature, typically 800 °C.

Here we report on the electronic properties, crystal structure and surface morphology of SiC films grown on Si(111)-7×7 reconstructed surface by means of C_{60} supersonic beams. Two beams with different fullerene kinetic

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energies have been used in order to investigate the role of the precursor energy on the physical and structural properties of the grown films. Surface electronic characteristics have been investigated *in situ* by Auger Electron Spectroscopy (AES) and X–Ray Photoelectron spectroscopy (XPS). Structural properties have been studied by Low Energy Electron Diffraction (LEED) and *ex situ* by Atomic Force Microscopy (AFM).

2 Experimental set-up and procedures

Experiments have been performed in an Ultra High Vacuum (UHV) apparatus made of two independent chambers. The beam is formed in a chamber with a base pressure $P_{\mathrm{base}} = 1 \times 10^{-7}$ mbar. The deposition, as well as the film characterisation, is performed in the main chamber in a clean and controlled environment ($P_{\mathrm{base}} = 3 \times 10^{-11}$ mbar).

Details of the beam source apparatus are described elsewhere [14]. The C_{60} source is essentially made of two coaxial quartz capillary tubes, resistively heated by a shielded tantalum foil. The beam energy calibration as a function of seeding buffer gas pressure (P_{seed}) and temperature (T_{sour}) can be found in references [15,16]. The experiments were carried out using He and H_2 as seeding gases: the corresponding fullerene particles kinetic energy is about 5 eV and 20 eV, respectively. C_{60} impinging rate ranging from 10^{13} to 10^{14} molecules/sec cm^2 have been used. Exposition time of substrates to the two different supersonic beams have been chosen in order to obtain comparable film thickness, assuming the same sticking coefficient for the two different C_{60} kinetic energies. The supersonic beam is perpendicular to the Si surface.

The main μ–metal chamber is equipped in order to perform several electron spectroscopies for surface physical and chemical characterisation, such as Auger electron (AES) and X–Ray Photoelectron (XPS) spectroscopies; low energy electron diffraction analysis (LEED) can be done as well. The electron energy analyser, a VG CLAM2 hemispherical analyser, has a resolution ranging from 0.1 eV (XPS) to 0.5 eV (AES). *Ex situ* morphological characterisation has been carried out with an Atomic Force Microscope (AFM) from Digital Instrument (Nanoscope Multimode IIIa) operated in air. Auger emission has been stimulated using a primary electron beam with kinetic energy of 3 KeV, while photoelectron spectra have been taken using photon energy of 1486.6 eV. The substrate used, a Si(111) wafer with resistivity 0.0120 Ωcm, was cleaned by a modified Shiraki procedure described in more details elsewhere [13]: after three cycles of oxidation in HNO_3 bath and hydrogenation in a 2.5% HF solution, the sample is rinsed in deionized water and finally oxidised in a HNO_3 for 10 min at 120 °C. The sample is inserted in the main chamber through a load-lock system. The silicon oxide film is removed by several annealing cycles, until a Si(111)- 7×7 surface reconstruction is obtained, as checked by a sharp LEED pattern.

SiC films have been grown at a substrate's temperature of 800 ± 5 °C and at a pressure lower than 2×10^{-10} torr. The Si(111)-7×7 surface cleanliness was checked by AES and XPS technique. After deposition, no further thermal annealing have been performed.

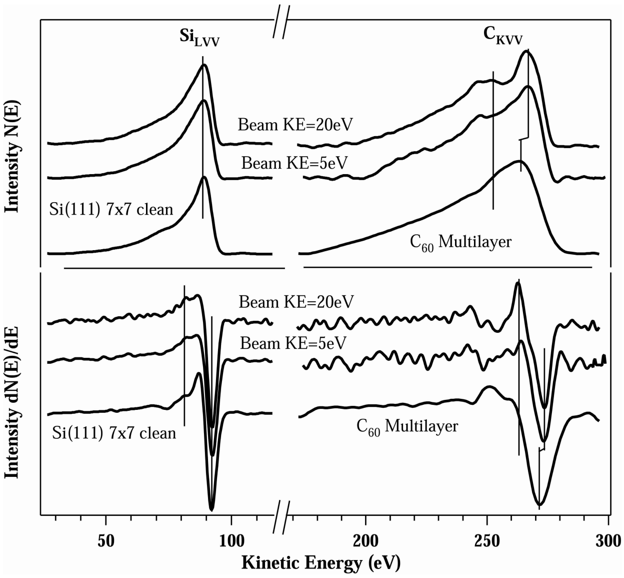

Fig. 1. Auger emission *vs.* electron kinetic energy from a clean Si(111)-7×7 surface, a C_{60} multilayer and the SiC films grown using 5 eV and 20 eV supersonic fullerene beams, as indicated in the figure. Upper panel shows spectra in integral mode, while lower panel shows same spectra but in analytical first derivative mode.

3 Results and discussion

The Auger lineshape of both Si $L_{2,3}$VV and C KVV peaks, whose main features are located at 92 eV and 274 eV respectively, is shown in Figure 1 for SiC films grown using both 5 eV and 20 eV supersonic beams. While spectra have been taken in the integral mode (Fig. 1 upper panel), the first order derivative spectra obtained by analytical methods (Fig. 1 lower panel) are also shown to better emphasise differences between lineshapes. All spectra are background subtracted and plotted against electron kinetic energy. For a comparison, Auger emissions from a Si clean surface and from a C_{60} multilayer film are also shown.

The SiLVV lineshape of Auger peak from the grown films does not show dramatic changes if compared to the emission from the clean surface. However, an additional structure in the 80–84 eV region is present, as can be clearly identified in the first derivative spectra. This feature is an evidence of the formation of the Si-C covalent bond [17–21]. No important differences between the two films signal can be identified.

Auger emission from a C_{60} multilayer is characterised by a main feature at 271 eV, with broad loss structures in the lower energy region. Carbon KVV signal from both films shows an energy shift of the main peak of about 2.3 eV towards higher energies, while the 250 eV–265 eV energy region is strongly modified. These are evidences of the formation of the Si-C covalent bond [18,20], with no significant differences between the two films.

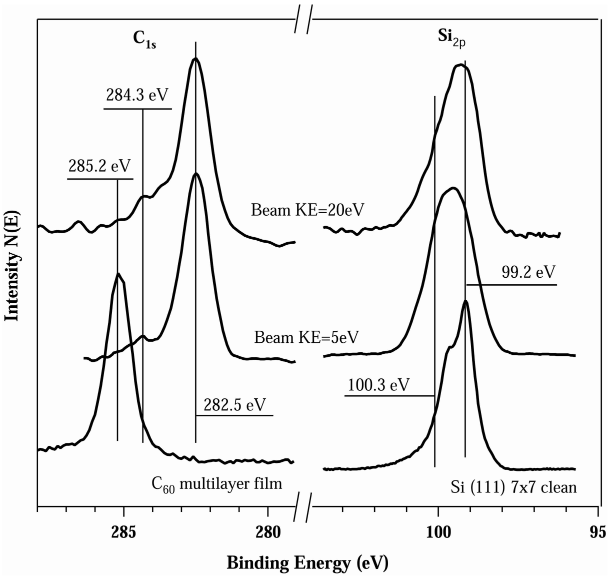

Fig. 2. X–ray photoelectron spectra *vs.* binding energy for the C_{1s} and the Si_{2p} core levels, from a clean Si(111)-7×7 surface, a C_{60} multilayer and the SiC films grown using 5 eV and 20 eV supersonic fullerene beams, as indicated in the figure.

AES analysis suggests the presence of SiC for films grown by means of both 5 eV and 20 eV fullerene supersonic beams. A quantitative characterisation of the composition of our films has shown the presence of a C rich surface, partially ascribable to the presence of unbonded C clusters or not opened C_{60} cages [21,22], as we will see in the following.

XPS spectra of the C 1*s* and Si 2*p* core levels are shown in Figure 2, for both films grown by 5 eV and 20 eV supersonic beams. As a comparison, photoelectron emissions from a C_{60} multilayer film and a clean Si(111)-7×7 reconstructed surface are also shown. Spectra are background subtracted and plotted against electron binding energies.

For the C $_{1s}$ core level emission from a C_{60} multilayer a value of 285.2 eV has been found. Spectra from film grown by 5 eV and 20 eV supersonic beams are characterised by a main feature at 282.5 eV, while a weak structure is present at about 284.3 eV. No other important differences are present between emissions from the two films. Analysis of C_{1s} core level emission puts in evidence very well the bonding state of the carbon atom. In fact, while emission from a C_{60} multilayer film, as well as from graphitic carbon is located at a binding energy from 284.9 eV to 285.3 eV, the presence of opened or deformed C_{60} cages is characterised by a shift towards lower binding energies, at about 284.2 eV–284.5 eV [22–24]. These fullerene particles are structurally modified by the presence of several Si-C bonds, with a deformation being larger with the increasing number of covalent bond [23]. A further decrease of the binding energy at 282.5 eV is a fingerprint of the Si-C covalent bond formation. Our experiments give clear evidence that SiC films have been grown using both 5 eV and 20 eV supersonic beams, with a presence of about 6–7% of partially unbound C atoms (referred to the total amount of carbon on the surface).

The Si_{2p} core level spectrum from a clean Si(111)-7×7 surface is characterised by the $2p_{1/2}$ and $2p_{3/2}$ doublet features, split by 0.6 eV. The Full Width at Half Maximum (FWHM) is about 1.0 eV. A more detailed lineshape analysis could provide information about the surface structure [25,26] and the type of the Si atoms involved in the interface formation, but this is beyond the scope of this study. Photoelectron spectra from the synthesised films are characterised by a line broadening in the higher binding energy region: FWHM are about 1.5 eV and 1.6 eV for the film grown by the 20 eV beam and 5 eV, respectively. The broadening is due to the presence of a new structure, located at about 100.3 eV and related to the presence of a SiC compound. This is confirmed by the energy difference between the C_{1s} and Si_{2p} core level of the atoms involved in the covalent bond formation: we found a value of 182.2 eV, in good agreement with the value of 182.3 eV for a SiC crystal [23,27]. The differences between Si_{2p} lineshapes from the two films, that apparently seem to indicate a more intense Si-C bounded structure for the film grown by the 5 eV C_{60} supersonic beam, are probably due to a different thickness between the two films. Results from both films can be considered almost equivalent, also taking into account analysis of C_{1s} core level emission and of Auger lineshapes.

The analysis of the surface electronic properties of the two films grown with supersonic C_{60} beams having different kinetic energies suggests that, in both cases, the Si-C covalent bond formation is strongly favored by a kinetic activation process, even at the low substrate temperature of 800 °C. No remarkable differences have been observed between the two SiC films. The film surface is carbon rich due to the presence of deformed fullerene cages or carbon aggregates, thus suggesting an excess of carbon on the film surface. This feature can be probably minimized reducing the film growing rate, that is reducing the impinging rates of the C_{60} beam. After post-annealing treatment at about 500 °C, we have observed a strong reduction of the carbon amount on the film surface. Taking into account that the sublimation temperature of C_{60} is around 400 °C, this confirms our hypothesis on the origin of the exceeding quantity of carbon.

Morphological studies have been carried out *ex situ* using an AFM operated in-air. In Figures 3a and b are shown 10 μm × 10 μm images of the film surface grown using the 5 eV and 20 eV supersonic C_{60} beams, respectively. The maximum thickness of both films has been evaluated to be around 20 nm.

The dark areas represent the typical defects, *i.e.* voids, that are characteristic of SiC on Si [28]: the depth of these voids have been evaluated to be around 20 nm, their base being probably the Si surface. This means that these area have not been interested by the coalescence process of the growing SiC islands. The typical shape of these defects is triangular for the Si(111) substrate [29], but in our film voids have irregular shape. Both films show the same voids density.

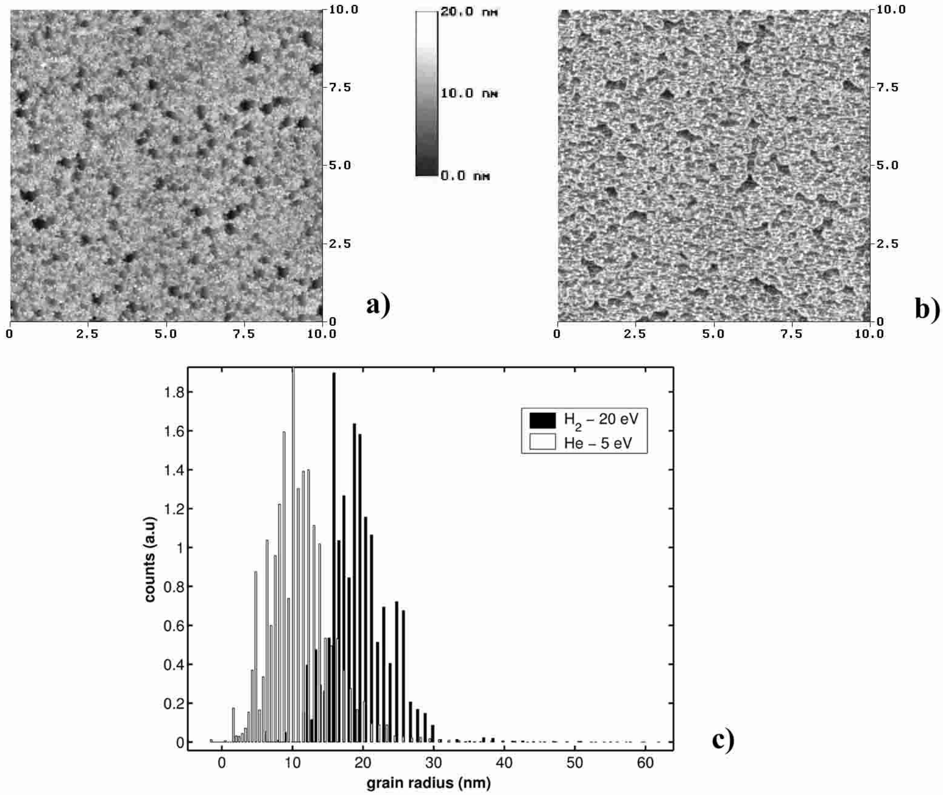

Fig. 3. Tapping-Mode Atomic Force Microscopy images (10 μm × 10 μm scan area, 20 nm vertical scale) of the SiC films grown on Si(111)-7×7 surface using a 5 eV (a) and 20 eV (b) supersonic fullerene beam. The root mean square roughness over the overall area ranges from 2.7 nm to 4.6 nm for a) and b) respectively (see text). c) Grain diameter distribution of the films grown with the 5 eV and 20 eV beams, calculated with an home-made pattern recognition software.

The smallest white dots have been interpreted as aggregation of C_{60} clusters [30], but analysis in this sense is still under development. However, this interpretation is in good agreement with results of AES and XPS, where the presence of partially bonded carbon clusters has been suggested.

The films have polycrystalline properties: surface morphology is characterised by a granular structure, that has been quantitatively analysed with a home-made pattern recognition algorithm. In Figure 3c the grain size distribution of films grown with 5 eV and 20 eV fullerene kinetic energy are shown. Distributions are lognormal with mean grain radii of 10 nm and 20 nm, accordingly, and the same geometric standard deviation: $\sigma = 1.15$ nm. Film root mean square roughnesses, measured over a 10 μm × 10 μm scan area, are 2.7 nm and 4.6 nm for the 5 eV/20 eV HSB grown film, respectively. These values include the effects due to voids, all other defects as well as the presence of unreacted fullerenes. The largest grain size and the higher roughness of the film grown using the highest energy C_{60} supersonic beam suggest a more efficient carbidisation process for this SiC film with respect to the other.

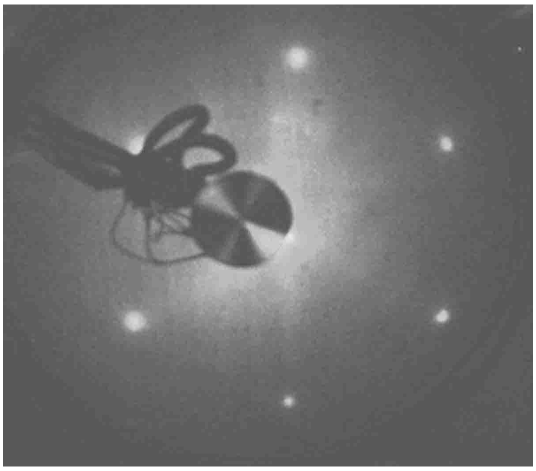

Fig. 4. LEED pattern from the film grown using the 5 eV C_{60} supersonic beam. Electron energy is 50 eV.

Structural properties have been investigated *in situ* by LEED technique. The observed pattern for the film grown using the 5 eV supersonic beam is shown in Figure 4 (50 eV electron energy). Although the electron diffraction analysis has been carried out also on the other film, the pattern is not shown as it has similar properties. The LEED pattern is typical of a cubic SiC, a clear hexagonal pattern with a weak diffuse background. A comparison of the single cell dimension suggests a reduction of about

20% with respect that of the Si(111)-7×7 surface, in good agreement with structural properties of SiC [1,13,18]. No presence of extra spot was found, as well as no signal from the Si surface has been detected. This suggests a film thickness of several monolayers, in good agreement with the thickness of about 20 nm estimated by means of AFM analysis. The weak background probably comes from the upper film surface, where unreacted carbon aggregates are still present, or from the Si free substrate. Concerning the structure of this uncovered Si surface, it is likely that it does not keep the original 7×7 order: those regions are the ones from which the Si needed to form the carbide comes from, through a process similar to etching so that the local atomic order results strongly affected. Moreover, presence of disordered carbon particles on these portions of the surface cannot be excluded. Both these effects affect the LEED patterns and explain why the unreacted Si surface does not lead to the sharp features that would be otherwise expected.

The presence of a surface order for the SiC film grown at a substrate temperature of 800 °C, as shown by LEED analysis, is an evidence of the influence of the precursor kinetic energy on the structural properties. While carburisation using C_{60} as a precursor has been reported even at 800 °C [19,22,23,25], no electron diffraction or crystal grain formation has ever been observed. The presence of a polycrystalline surface, as shown by AFM analysis, suggests the presence of several different domains for the observed cubic phase: however, it has not been possible to put in evidence such a feature by LEED images.

4 Conclusions

SiC thin films have been grown in UHV from a clean Si(111)-7×7 surface using hyperthermal supersonic beams of C_{60}, at two different kinetic energies: 5 eV and 20 eV. The substrate temperature was 800 °C. Films have been characterised, *in situ* and *ex situ*, by using surface electron spectroscopies, like AES and XPS and by means of LEED and AFM.

Physical/chemical analysis shows that SiC thin films have been produced. No significant differences between the structures of the two films have been found. The morphology of the films and, in particular, the granularity is influenced by the fullerene deposition energies. On both films a small amount of unreacted carbon aggregates is still present on the surface, leading to a carbon rich film surface. This feature can be probably reduced with a lower C_{60} beam impinging rates.

Structural analysis reveals an ordered polycrystalline surface, a property usually not find in SiC film grown using other fullerene deposition techniques at a substrate temperature of 800 °C. This confirms the role of the precursor kinetic energy, which influences both the film physical and structural properties. The formation of the Si-C covalent bond is possible by mean of a kinetic activation process at 800 °C, while with other thermal evaporation technique temperatures of about 900 °C are necessary.

The larger grain size and roughness for the film grown using the 20 eV supersonic beam suggests that the higher the kinetic energy of the fullerene particles, the higher the efficiency of the growth process.

Studies are under development to grow SiC films at lower substrate temperatures, in order to reduce the efficiency of the Si diffusion process and, consequently, the voids size and density. A study of the initial growth states should provide new elements for the understanding of the role of kinetic energy for the Si-C covalent bond formation, the highlands structural properties and possibly a procedure for complete coalescence.

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