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# PHOTOEMISSION STUDY OF SiC FILMS GROWN ON Si WAFERS BY USING $C_{60}$ PRECURSORS

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*One possible way to grow crystalline silicon carbide (SiC) on Si (100) is to deposit fullerene molecules followed by an annealing at temperatures higher than 800°C, where the $C_{60}$ molecule breaks. In this paper we present the photoemission study results on these films. X-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS) show the SiC formation and evolution, when the annealing temperature is varied between 800°C and 850 °C. Crystalline and relaxed films were obtained by annealing at 850 °C. For these films, the valence band spectra given by UPS measurements show similar features as for crystalline SiC bulk.*

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## 1. Introduction

Currently, silicon is used to build microelectromechanical systems (MEMS) which include: motors, sensors, resonators and actuators. In order to improve the mechanical and electrical properties, there are a lot of studies on the new materials. Silicon carbide (SiC) is not a new material but is a potential one that can be used to enhance the MEMS' mechanical and electrical properties. Its hardness and electrical behaviour recommend it as one of the solution to extend the lifetime of these devices. The SiC films can be also used as a thin buffer layer for the growth of diamond films on silicon substrates [1-3]. The most used deposition technique for crystalline SiC layers on silicon substrates is chemical vapour deposition (CVD). Although many studies were done in order to understand the growth mechanisms and the parameters that influence in a great measure the films' properties, there are still two main inconvenients to be solved: i) high substrate temperature values (>1050°C) are required by CVD techniques, and ii) the mismatch between the lattice constant of silicon (5.43 Å) and of silicon carbide (4.34 Å) produces high values of the interface density of states and of the material stress. Several authors have demonstrated that SiC films can be obtained on silicon substrates via fullerene precursors [3, 4 - 6]. Using fullerenes to grow silicon carbide films is advantageous because the $C_{60}$ molecules do not introduce unwanted species into the film structure. The thermal reaction of $C_{60}$ molecules with Si (111) and/or Si (100) surface was studied by various techniques [7, 8]. In this way, the chemical bonding of the first $C_{60}$ molecules' layer on Si (100) surface was proved [7], while the interaction between $C_{60}$ molecules is of van der Waals type for $C_{60}$ island grown on Si (111). In this paper we report on the formation of SiC films by thermal reaction of fullerenes' molecules with the Si (100)-(2×1) surface. The effect of the annealing temperature on the c-SiC formation is shown. X-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS) were performed in-situ in order to characterise the obtained layers.

## 2. Experiment

Our study was performed on one monolayer (1ML) of $C_{60}$ samples prepared by thermal evaporation of the powder provided by MER Corporation. As substrates we have used $4\times20$ $mm^2$ (100) silicon wafer with $\rho=1.44-2.16$ $\Omega$cm. The pressure in the deposition chamber was less than $10^{-10}$ Torr, and during evaporation, in the standard process, $2\times10^{-8}$ Torr. This deposition chamber is part of a multichamber ultra-high-vacuum (UHV) system equipped with a silicon chemical vapour deposition chamber, X-ray photoemission spectroscopy (XPS) equipment and ultraviolet photoemission spectroscopy (UPS) equipment. The vacuum into each part of the UHV system is monitored.

In order to obtain a very clean surface, the substrate was cleaned after a procedure which consisted in: I) more than 10 hours of heating at 500 °C in vacuum; II) 10 min at 1150 °C in $H_2$ atmosphere in order to remove the protective oxide and any atom adsorbed at the silicon surface; III) CVD deposition of a thin layer of silicon from $SiH_4$ at 850 °C, 30 min; IV) the cooling of the sample in $SiH_4$ atmosphere.

This substrate is transferred through the UHV tunnel into the $C_{60}$ deposition chamber. Before, the $C_{60}$ powder loaded into the crucible was outgassed at 300 °C for many hours. The amount of the evaporated $C_{60}$ was determined during deposition process with a quartz-crystal thickness monitor. During evaporation, the substrate temperature was maintained at 250 °C in order to ensure that only 1 ML of the $C_{60}$ be deposited at the silicon surface. The evaporation process is stopped before the end of heating and, during this time the $C_{60}$ multilayers desorbe from the silicon substrate excepting the first one that is strongly bound and ordered on the (100) Si surface.

The SiC surface is obtained by direct thermal reaction of Si (100) substrate atoms with the adsorbed $C_{60}$ molecules. The annealing process at temperature higher than 800 °C produces regions with SiC alloys. We have obtained c-SiC on the all-surface substrate for annealing at 850 °C.

Photoemission spectroscopy is a powerful tool for investigating the materials' electronic structure. XPS and UPS spectroscopy were used for studying the surface properties. Taking into account that every distinct bond from material structure is characterised by a specific electron arrangement of the most external atomic shell, using the XPS, both the qualitative (the presence of the chemical element) and the quantitative determinations can be done. XPS measurements were performed with a monochromatized ( $h\nu = 1486.6$ eV ) ESCA system equipped with hemispherical electron-energy analyser. The photon source is the $K_\alpha$ line of aluminium and the resolution of the system is 0.35 eV.

UPS measurements were recorded with a double-pass cylindrical mirror analyser. A double grating monochromator was used in order to monochromatize the Xe lamp light. The resolution of the system is 70 meV. The Fermi level position was determined by measuring the UPS spectrum of a freshly evaporated gold layer.

## 3. Results and discussions

Fig. 1 shows the Si 2p core level lines for as-deposited $C_{60}$ molecules on clean Si (100) surface and annealed samples at different temperatures. The Si-2p doublet has the first peak, assigned to electron kinetic momentum m=3/2, placed at $99.56\pm0.02$ eV, whereas the second one, assigned to m=1/2 is placed 0.6 eV to the right side ($100.16\pm0.03$ eV). During the annealing process, the silicon atoms diffuse to the $C_{60}$ surface, break the C – C bonds and form Si – C bonds. As a function of the temperature values, the $Si_xC_{1-x}$ alloy that is formed should have various values of the x parameter. When each carbon atom is surrounded by 4 - silicon atoms and each silicon atom has as the nearest neighbour 4-carbon atoms, the $Si_{0.5}C_{0.5}$ alloy is obtained. We found that crystalline SiC appears for annealing temperatures higher than 850 °C [9]. As can be observed from the Fig. 1, the annealing at 800 °C produces modifications in the XPS spectra. A tail appears on the Si 2p spectrum towards the higher binding energy values. The higher the annealing temperature, the wider is the spectra tail.

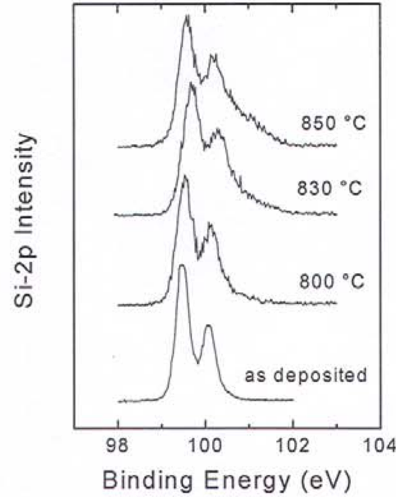


*Fig. 1 XPS spectra of the Si 2p core level for sample with $C_{60}$ as-deposited and samples annealed at temperatures higher that 800 °C.*

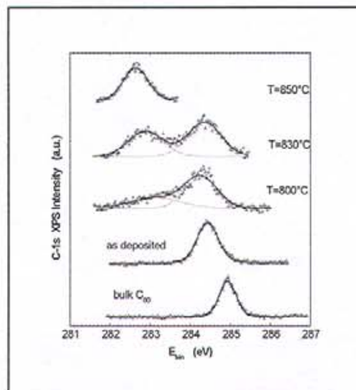


*Fig. 2 Gaussian fit of the C 1s core level. It is shown the evolution of the band assigned to the SiC entities, when the annealing temperature is increased.*

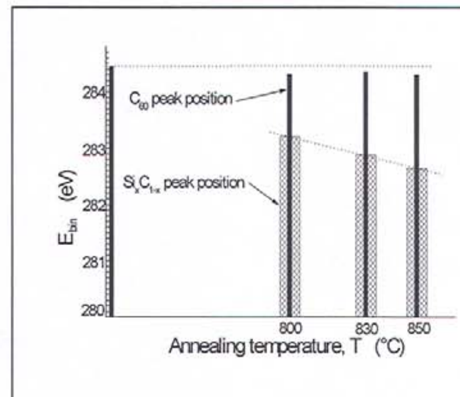


*Fig. 3 The peaks' positions for both the $C_{60}$ and $Si_xC_{1-x}$ gaussians used in the fit from the Fig. 2.*

These structural modifications are more evident in Fig. 2 where the C 1s core level spectra are presented. The first spectrum is due to the bulk $C_{60}$ and it is characterised by a peak placed at 284.93 eV. The second spectrum shows the interaction effect of the carbon atoms from the $C_{60}$ molecules with silicon atoms from substrate surface: the C 1s core level is shifted at $284.68 \pm 0.02$ eV. For the sample annealed at 800 °C, it appears a new peak on the C 1s core level spectrum. This was assigned to the C-Si bonds and its efficiency on the C 1s spectra increases with the increase of the annealing temperature. We fitted these spectra with two gaussian components: one for the carbon atoms from the $C_{60}$ molecules and the other one for carbon atoms from SiC entities. As

can be seen in Fig. 3, the peak position for carbon in fullerenes' molecules is constantly placed at 284.4 eV, whereas the position of the peak assigned to the c-Si bonds is shifted to low values with the increase of the annealing temperature. We suppose that this variation is due to the different species of $Si_xC_{1-x}$ alloys, which are formed at different temperatures. Annealing at T = 850 °C pins the peak position of the C-1s core level at 282.6 eV.

Fang and Ley [10] have developed a model for the determination of the chemical shift of the Si 2p and C 1s core levels, when silicon carbide is formed. Using the same notations, we can calculate for samples annealed at 850 °C:

$$\Delta E_2 = E(C\text{-}1s) - E(Si\text{-}2p) = 282.57 - 100.32 = 182.25 \text{ eV} \quad (\text{error: } \pm 0.06 \text{ eV})$$

which is in good agreement with $\Delta E_2' = 182.3 \pm 0.2$ eV obtained on the crystal SiC [11]. As concerned the first coordination, a similar structure as in crystalline SiC was obtained. Using (RHEED) method (reflection high energy electron diffraction) we have found that the SiC structure is cubical and (100) oriented [9].

The SiC peaks' area from the Si–2p and C-1s XPS core levels could be used to determine the structural parameter, x. If we consider different $Si_xC_{1-x}$ groups as structural entities, a $x_{eff}$ value could be calculated: for N structural entities, the SiC peak in the silicon spectrum is due to the electrons that belong to $N(1-x_{eff})$ atoms. Therefore, the area under the SiC peak is $A_{SiC}^{Si} \approx N(1-x_{eff})S_{Si}$, where $S_{Si}$ is the atomic sensitivity factor for silicon. Following a similar way, the area under the SiC peak in the carbon spectrum is $A_{SiC}^{C} \approx N x_{eff} S_c$, with $S_C$ - the atomic sensitivity factor for carbon. After a simple mathematical procedure, it results:

$$x_{eff} = \frac{S_C A_{SiC}^{Si}}{S_C A_{SiC}^{Si} + S_{Si} A_{SiC}^{C}} \quad (1)$$

For $S_{Si} = 0.17$ and $S_C = 0.207$, [12], the obtained $x_{eff}$ values are 0.84, 0.64 and 0.56 when the annealing temperatures were 800 °C, 830 °C and 850 °C respectively. The sample annealed at 800 °C shows an $x_{eff}$ value coresponding to more silicon due to the chemically bonded carbon atoms from $C_{60}$ cage with atoms from substrate. At this temperature the fullerenes' cages are maintained but more and deformed bonds between $C_{60}$' carbon atoms and silicon substrate are formed. Moreover, the silicon atoms are diffusing from the substrate surface and bond the carbon atoms surrounding the $C_{60}$ cage.

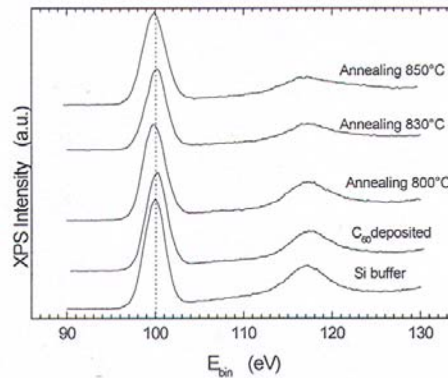


*Fig. 4 Plasmon losses from the XPS spectra in the Si 2p region. The plasmon frequency for sample with $C_{60}$ as-deposited is corresponds to 17.58 .eV, while for SiC samples corresponds to 17.33 eV.*

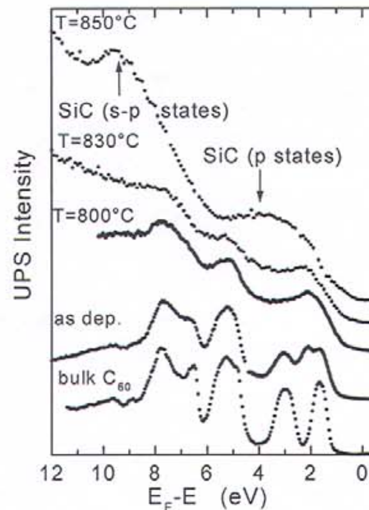


*Fig. 5 UPS spectra and their evolution with annealing temperature. The valence band of the SiC films has a p – character.*

By increasing the annealing temperature, the diffusion of the silicon atoms is accelerated and the possibility to break the C-C bonds from the $C_{60}$ balls' surface is higher. Taking into account that silicon carbide was obtained on the whole surface for annealing at 850 °C, we suppose that for 830 °C locally, the temperature fluctuations yield SiC islands. At 850 °C the fullerene cages are completely broken and the carbon and silicon atoms find equilibrium positions, thus giving rise to a SiC relaxed structure.

The bonds' nature could be studied from the plasmon losses observed in the XPS spectra. In Fig. 4 are shown the plasmon peaks from the Si 2p core level region, all spectra being arbitrarily aligned to the main core-level line. The bonds between silicon atoms from the surface and the carbon atoms from $C_{60}$ molecules are pointed out by the shift of the plasmon peak position: 17.29 eV for the silicon buffer layer as-grown and 17.58 eV for 1ML $C_{60}$ deposited on the silicon surface. Yajima and Tsukada [ref.14 from K. Sakamato et al., [4]] have shown a hybridisation between the $C_{60}$ molecules and surface silicon atoms. At 800 °C the plasmon peak is placed at 17.72 eV. We believe that the annealing at this temperature doesn't change drastically the bonds' nature, but a higher number of silicon atoms is involved in this type of bonds. A great modification appears for the samples annealed at 830 °C and 850 °C where the plasmon frequency is 17.4 eV and 17.33 eV, respectively. Now, the material structure is changed. Most carbon atoms are bonded to silicon atoms and form SiC. This was proved by high-resolution XPS spectra. The free electrons that oscillate with plasmon energy arise, from the defects of the SiC entities. As can be seen, the width of the gaussian curve is larger than that of the pure silicon, or of silicon bonded with $C_{60}$. The tail that appears on the right hand side of the spectrum could be due to the dumping oscillation given by inelastic scattering. At 850 °C, when the SiC layer is formed, the bonds' nature could change from ionic one, which exists between $C_{60}$ and atoms from the silicon surface, to a covalent one.

It is known that the valence electrons are the most sensible to electron states of the bonding type. The information about the density of states distributed below the Fermi level could be obtained by using the UPS measurements. Fig. 5 shows the UPS spectra of the investigated samples. The bottom spectrum is given by the bulk $C_{60}$ and the more important bands are the highest occupied molecular orbitals (HOMO) and respectively HOMO-1. The chemical bond between $C_{60}$ molecules and silicon atoms is shown by a new peak placed at 2.2 eV between the HOMO and HOMO-1 bands [7]. The UPS spectra of the annealed samples show that both the intensity and the width of this peak

increase, while the HOMO and HOMO-1 structures broaden off. These could be related to the $C_{60}$ cage deformation and many carbon atoms interact with the silicon atoms from the substrate. At high temperature, the mobility of the silicon atoms is increased and the ability to bond the carbon from the $C_{60}$ molecules is higher. As can be observed in Fig. 5, if at T = 830 °C there are reminiscences of the HOMO band, at T = 850 °C the UPS spectra reproduce the c-SiC valence band. This is supported by the band of 4 eV and of 9 eV, which have, after Wagner et al. [12], a "p" character and "s-p" character, respectively [13]. The shape of the UPS spectrum and the positions of these two bands, prove the formation of SiC in our films.

## 4. Conclusions

We have prepared and investigated silicon-carbide thin films on Si(100) substrates by a carbonisation process using $C_{60}$ molecules as precursors. The results can be summarised as follows:

I) c-SiC was obtained from $C_{60}$ deposited on Si (100) and annealed at 850 °C;

II) small amounts of different $Si_xC_{1-x}$ alloys began to appear with annealing at 800 °C. The SiC peak position from C 1s core level was shifted from 283.4 eV to 282.6 eV when the annealing temperature was varied from 800 °C to 850 °C. This allowed us to imagine a model for the carbonisation process;

III) the UPS measurements have proved the formation of chemical bonds between $C_{60}$ molecules and silicon atoms by the appearance of a new peak placed at 2.2 eV from the Fermi level position, between HOMO and HOMO-1 bands;

IV) for samples annealed at 850 °C, both the XPS and UPS spectra show similar features as in the case of bulk c-SiC.

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## References

[1] Wang E.G., Physica **B 185**, 85(1993).
[2] Balooch M., Hamza A.V., J. Vac. Sci. Technol. **B 12**, 3218(1994).
[3] Hamza A.V., Balooch M., Moalem M., Surf. Sci. **317**, L1129(1994).
[4] Sakamoto K., Suzuki T., Harada M., Wakita T., Suto S., Phys. Rev. **B 57** (15), 9003(1998).
[5] Sakamoto K., Suzuki T., Wakita T., Suto S., Hu C. W., Ochiai T., Kasuya A., Appl. Surface Sci. **121/122**, 200(1997).
[6] Levinson J. A., Hamza A.V., Shaqfeh E.S.G., Balooch M., J. Vac. Sci. Tech. **A 16** (4), 2385(1998).
[7] De Seta M., Sanvitto D., Evangelisti F., Phys. Rev. Lett. (in press).
[8] Xu H., Chen D. M., Creager W.N., Phys. Rev. Lett. **70**, 1850(1993).
[9] De Seta M., Tomozeiu N., Sanvitto D., Evangelisti F., paper presented at INFM Conference, Catania, Italy, 1999.
[10] Fang R.C., Ley L., Phys. Rew. **B 40** (6), 3818(1989).
[11] Mélinon P., Kéghélian P., Perez A., Ray C., Lermé J., Pellarin M., Broyer M., Bondeulle M., Champignon B., Rousset J.L., Phys. Rev. **B 58** (24), 16481(1993).
[12] Wagner C.D., Riggs W.M., Davis L.E., Moulder J.F., Muilenberg G. E. in Handbook of X-ray photoelectron spectroscopy, Perkin-Elmer Corporation, 1979.
[13] Chen D., Workmanand R., Sarid D., Surf. Sci. **344**, 23(1995).