Silicon Overgrowth of Fullerene C_{60}

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Abstract
In this study, the silicon (Si) overgrowth of fullerenes (C_{60}) was investigated using scanning tunneling microscopy (STM). It could be shown that monocrystalline overgrowth of C_{60} on Si(100) and Si(111) surfaces is possible up to a fullerene coverage of 50%. At higher coverages, only polycrystalline overgrowth can be achieved. During overgrowth, segregation of a small percentage of fullerenes could be observed. Upon thermal treatment of the overgrown fullerene structures, nanometer-sized silicon carbide (SiC) islands were formed which could be measured by STM and X-ray photoelectron spectroscopy (XPS).

1. Introduction

Chemical and physical properties of fullerenes, especially those of the Buckminsterfullerene C_{60}, have been the subject of intensive studies since their discovery by Kroto, Smalley et al. in 1985 [1, 2]. Scanning Tunneling Microscopy (STM) has shown itself to be an excellent tool for the analysis of the adsorption of fullerenes on varying surfaces and their interaction with these surfaces. For semiconductor surfaces, their interaction varies between weak for GaAs to very strong for Si [3]. We have used this strong interaction to fix single C_{60} to the surface and embed them in the Si crystal for possible electronical applications.

The possibility to produce SiC on Si surfaces from C_{60} as a precursor has been investigated by several groups in the last years [4,5]. In contrast to these studies, we start from sub-monolayer coverage with fullerenes and are able to create single-crystalline SiC nanodots by thermal treatment of the sample.

2. Experimental setup

The Omicron UHV system used in these studies has already been described in detail [6]. The STM is adjacent to a chamber for sample preparation and analysis (base pressure 1×10^{-10} mbar), equipped, among other components, with evaporators for Si, Ge, B and C_{60}, sample heating, LEED and AES.

The samples used are phosphorus-doped Si(100) and Si(111) wafers with resistivities ranging from 4 to 8 Ωcm. After chemical cleaning they were degassed in the UHV-chamber and then flashed to 1200°C by resistive current heating to remove the native oxide layer. A 2x1 or 7x7 reconstructed surface, depending on the type of substrate, was prepared afterwards. C_{60} powder was evaporated at a rate of 0.1 monolayer (ML) / minute. Some samples were then annealed using current resistive sample heating. Temperatures were monitored with an infrared pyrometer ($\Delta T \approx 2°C$). After every step of preparation, the sample surface was controlled using the STM.

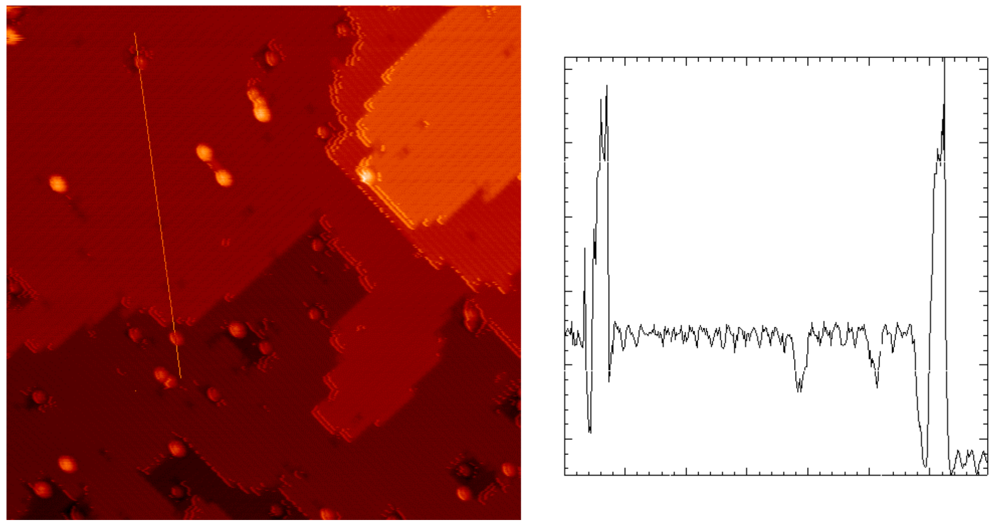
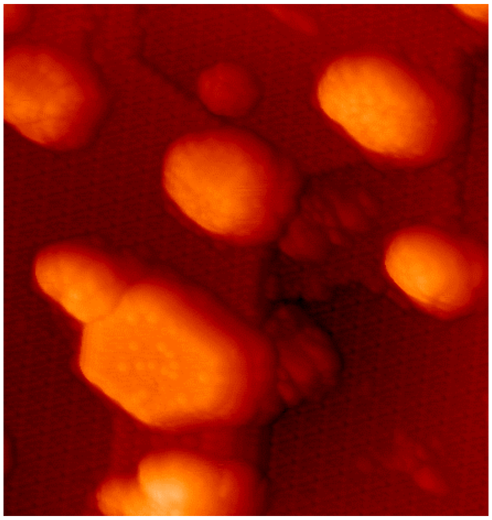


Fig. 1. C_{60} on Si(100) during overgrowth. A cut along the marked line shows embedded C_{60} and free C_{60} on lower terrace to have the same height (STM image size: 46×46 nm^2, tunneling voltage: -3 V)

All the STM images presented were obtained at a constant tunneling current of 0.2 nA and are shown in grey scale corresponding to the surface height.
The XPS measurements were conducted in a VG ESCALAB 250iXL Spectrometer, with a base pressure of 5 $\times 10^{-10}$ mbar. XPS Data were obtained using monochromatized Al Kα radiation at 1486.92 eV. Samples for XPS were overgrown with 5 nm of Si before transporting them into the XPS chamber.

3. Results and Discussion

When deposited on Si surfaces at room temperature, C_{60} interacts strongly with the dangling bonds of the surface. The fullerenes therefore stay statistically distributed on the surface and do not form ordered layers. In our studies, these single molecules were embedded in the Si crystal by overgrowing them with means of Molecular Beam Epitaxy (MBE) at a substrate temperature of 450°C for Si(100) and 650°C for Si(111). These temperatures were chosen on one hand to achieve good crystal quality and on the other hand to minimize surface diffusion of C_{60} which occurs at higher temperatures and negatively affects the overgrowth process.
STM measurements have shown that C_{60} up to a coverage of about 50% could be overgrown with a monocrystalline Si layer (Fig. 1). At higher coverages only polycrystalline growth could be achieved due to the high number of C_{60} molecules that act as defects. Ordered monolayers which were formed with the help of a boron surface phase [7,8] show the same polycrystalline top layers. Segregation of fullerenes during growth is very low, which has been confirmed by STM and SIMS measurements. The maximum solubility of C_{60} in crystalline Si was found out to be as high as $1{,}49\times10^{13}$ C_{60}/cm^2.
To form silicon carbide (SiC) from these structures of overgrown fullerenes, the samples underwent thermal treatment at temperatures ranging from 700°C to 1200°C. When imaging the surface with STM after annealing at different temperatures, one can observe increased surface diffusion and the formation of fullerene clusters starting at around 500°C for Si(100) and around 700°C for Si(111). At 800°C the C_{60} clusters start changing their structure into crystalline islands. This crystallization process is completed at around 900°C, when all the fullerenes have



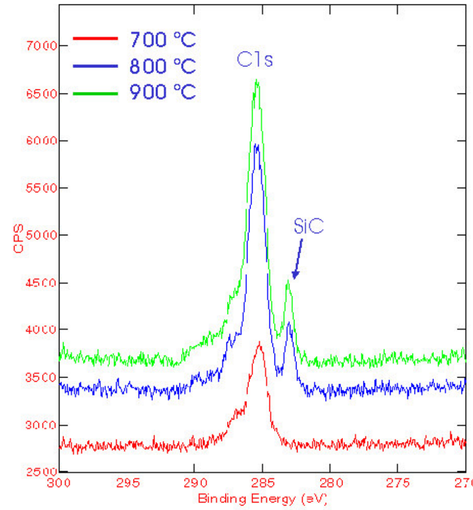


Fig. 2. a) SiC islands formed during thermal treatment at 900°C, underlying 7x7 reconstruction of Si(111). (STM image size: 46×46 nm^2, tunneling voltage: -3 V) and b) XPS spectrum of energies near C1s peak. SiC formation at 800°C and 900°C can be seen.

transformed into crystalline islands (Fig. 2.a). Around the islands, an increased step density compared to that of the untreated surface can be observed (Fig. 2.a).
This is one indication for the islands consisting of a different material than the substrate. Another indication derived from STM measurements are the reconstructions on top of the islands which are not at all typical for Si surfaces. XPS measurements confirm the existence of SiC in our samples after annealing at 800°C minimum (Fig. 2.b). Therefore, the observed islands can be identified as SiC islands. When the samples are annealed at 1200°C, carbon diffuses into the Si bulk (a process that is commonly used for surface cleaning) and after 15 minutes, the islands disappear completely.

Conclusion

We report the crystalline overgrowth of fullerene molecules with silicon. C_{60} up to a 50% coverage can be embedded in monocrystalline Si. Further, SiC nanodots could be formed by thermal treatment of the sample surfaces. These two new techniques open new possibilities for innovative semiconductor devices.

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