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Fullerene (C_{60}) Adsorption and Films Growth on the $(\sqrt{3}\times\sqrt{3})$ and (3×3) Surface of 6H SiC(0001)

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Abstract. Scanning tunneling microscopy (STM) was used to study the C_{60} adsorption on the Si rich (3×3) and C rich $(\sqrt{3}\times\sqrt{3})$ surface of 6H-SiC(0001). At room temperature, triangular or hexagonal islands commensurating to the substrate structure at submonolayer coverages were observed. One of the interesting observations was the nucleation of the second layer of the C_{60} molecules even at submonolayer coverages. On the (3×3) surface, multilayer growth of C_{60} with the close-packed fcc(111) structure was observed: while on the $(\sqrt{3}\times\sqrt{3})$ surface, for coverage higher than 1 ML, disordered surface morphology was observed. Epitaxial growth of SiC was also achieved using C_{60} as carbon source on 6H-SiC(0001) surfaces.

1. INTRODUCTION

Adsorption and film growth of C_{60} molecule on various semiconductor surfaces have been studied by STM in the past several years [1]. An important aspect of the research is to understand the adsorption geometry at the submonolayer regime and thin film growth mechanisms in the multilayer regime, and the interaction between the C_{60} and the substrate. In most of the cases being studied, the structure of the monolayer and multilayer films consists of the hexagonal close-packed (111) layer. The only exception being reported so far is the formation of a highly strained (110) oriented C_{60} film on GaAs (001) As-rich 2×4 β surface [2].

No study has been reported so far on the C_{60} adsorption on the SiC surface. In this work, we present our recent STM study of the C_{60} adsorption on the 6H-SiC(0001) $(\sqrt{3}\times\sqrt{3})$ and (3×3) surface prepared by in situ Si beam etching. It has been known that the 6H-SiC surface exhibits various phases, such as $(\sqrt{3}\times\sqrt{3})$, (2×3) , $(2\sqrt{3}\times 6\sqrt{3})$, and (3×3) , depending on the surface Si/C ratio. Among them, the $(\sqrt{3}\times\sqrt{3})$ structure is believed to be C rich and has very low corrugation (~ 0.2 Å), and the (3×3) structure is Si rich and has large corrugation (~ 2.5 Å), while their atomic structures are still not well-established [3,4]. An interesting adsorption behavior may be expected for the 6H-SiC (0001) $(\sqrt{3}\times\sqrt{3})$ and (3×3) surface, just like the case of GaAs (001) surface where two different phases, 2×6 and β -(2×4) produced quite different C_{60} films [2,5]. Further more, study of the adsorbate induced structures may provide valuable structural information on the SiC surface structures themselves.

2. EXPERIMENTAL

The details of the STM instrumentation and cleaning procedure of the SiC sample have been reported elsewhere [4,6]. Briefly, our "FI-STM" is a combination of STM and a room temperature field ion microscope (FIM) which was used for the precise characterization of the scanning tip. The (99.95%) C_{60} powder was put in a small Ta-made dispenser. Sublimation of the C_{60} molecules was performed by directly heating the C_{60} doser at 340 °C. The n-type 6H-SiC(0001) single crystals were supplied by Cree Research. The clean SiC surface was obtained by annealing the sample at 900-1000 °C in a flux of Si, which was produced by resistively heating a small Si wafer. The STM imaging was performed at room

temperature using the constant current mode with sample bias between -1.2 V and -2.5 V, unless otherwise specified.

3. RESULTS AND DISCUSSION

3.1 Adsorption at room temperature

Shown in Fig. 1(a) & (b) are the ($\sqrt{3}\times\sqrt{3}$) and (3x3) surface following deposition of approximately 0.02 ML of C_{60} . Each large bright quasi-spherical protrusion corresponds to an individual C_{60} molecule. It is shown that the C_{60} molecule adsorbed on top of the bright protrusion of the ($\sqrt{3}\times\sqrt{3}$) at empty-state image. For the (3x3) surface the C_{60} also adsorbed on top of the protrusions. On both surfaces, large area scans indicated no preference adsorption of the C_{60} molecules at step edges or defect sites. While most of the molecules are present individually on the surfaces, large area images showed that approximately 5% of the C_{60} s formed dimer (Fig. 1(a)). However, after the molecules find the most stable adsorption site they were very stable and showed no sign of diffusion. Even after annealing the surfaces to 300-400 °C, the population of the C_{60} dimers did not increase.

When the C_{60} coverage increased, the molecules nucleated into clusters of triangular or hexagonal shape, as shown in Fig. 1(c) & (d), after adsorption about 0.4 ML of C_{60} . By line-scan profile, it can be clearly seen that the C_{60} clusters are commensurate with the substrate structure on both surfaces. Referring to Fig. 1(d), the uncovered (3x3) domain, the first and second layer C_{60} cluster are labeled as (3x3), I and II respectively. One of the interesting observations at this coverage is that the second layer C_{60} molecules grown on top of the first layer.

Figure 1: STM images of the 6H-SiC(0001) surface after deposition of various amount of C_{60} at room temperature. (a) The ($\sqrt{3}\times\sqrt{3}$) surface with 0.02 ML coverage. The image size is (80Åx80Å), and sample bias is + 1.2 V. (b) The (3x3) surface (60Åx60Å) with 0.02 ML coverage. (c) The ($\sqrt{3}\times\sqrt{3}$) surface (300Åx300Å) with 0.4 ML coverage. (d) The (3x3) surface (320Åx320Å) with 0.4 ML coverage. (e) The ($\sqrt{3}\times\sqrt{3}$) surface (320Åx320Å) with 1 ML coverage. (f) The internal structure of the C_{60} on the ($\sqrt{3}\times\sqrt{3}$) surface imaged by STM. The image size is (160Åx160Å).

The ($\sqrt{3}\times\sqrt{3}$) surface after ~ 1 ML of C_{60} deposition is shown in Fig. 1(e). The second layer C_{60} islands grew without completion of the first layer, leaving open space in the first layer. Similar behavior was also observed on the (3x3) surface. Another interesting observation was that the C_{60} intramolecular structure can be imaged on both first and second layer. It can be seen (Fig. 1(f)) that three stripes are running parallel within the individual molecular image, which indicates that the self-rotation of the individual C_{60} molecules has stopped. This intramolecular structure is very similar to those observed for the C_{60} adsorption on the Si surface where three or four stripes were observed on the first layer of the C_{60} film [1].

To appreciate the adsorption behavior of the C_{60} molecule on the 6H-SiC(0001) ($\sqrt{3}\times\sqrt{3}$) and (3x3) surface, we show in Fig.2 model of the C_{60} molecules adsorption site and formation of dimer on those two surfaces based on the STM results. The C_{60} adsorb at the center of the vacancy of the ($\sqrt{3}\times\sqrt{3}$) structure [4], while a satisfactory atomic mode is not yet available for (3x3) surface, only a schematic diagram of the (3x3) geometry is shown. On the ($\sqrt{3}\times\sqrt{3}$) surface, when a arriving C_{60} molecule approaches the existing C_{60} the best bonding site for the molecule are the second closest neighbors since the closest neighbors are too close (5.3 Å away). Then the C_{60} dimer will have with separation of $2\sqrt{3}$ lattice spacing of SiC(0001)-(1x1), i.e., 10.7 Å. In the case of (3x3) surface, the ideal C_{60} dimer separation is 9.3 Å. One previous theoretical study [8] has shown that the equilibrium bond length for a C_{60} dimer is 9.84 Å. Compared with the respective dimer model, the intermolecular spacing is then about 9.1% larger on the ($\sqrt{3}\times\sqrt{3}$) surface, but about 5.5% smaller on the (3x3) surface. Therefore, on the ($\sqrt{3}\times\sqrt{3}$) surface the C_{60} dimers are under tensile stress while they are under compressive stress on the (3x3) surface. It is interesting to compare our observation of the adsorption behavior of the C_{60} on the ($\sqrt{3}\times\sqrt{3}$) and (3x3) surface of 6H-SiC(0001) with the previous reported results on the Si(100)-(2x1), Ge(100)-(2x1) and GaAs(001)-(2x4)As surfaces [2,7], where the substrate structures were also found to play a critical role in determining the initial adsorption and film growth of the C_{60} . In the case of Si(100) and Ge(100) surface the (2x1) reconstruction forms trough in between the dimer rows, which confines the C_{60} molecules so that they are unable to adopt the closed hexagonal packing. Instead, the C_{60} molecules form a rhombic lattices that has the c(4x3) structure [7]. While for the adsorption of C_{60} on the anisotropic and strongly corrugated GaAs(001)-(2x4)As surface, a molecular chain consisting of the C_{60} dimer was confined to the troughs of the substrate at the initial adsorption of C_{60} , and this pair-chain structure serves as a template for growth of the "strained" van der Waals C_{60} fcc(110) overlayer [2]. In the present case of the ($\sqrt{3}\times\sqrt{3}$) and (3x3) surface of the 6H-SiC(0001), it also demonstrates that the substrate structures and site-specified C_{60} -substrate interaction play a leading role in the adsorption and film growth. The constrains provided by the substrate resulted in the formation of the stressed C_{60} dimer on both surface. But on the ($\sqrt{3}\times\sqrt{3}$) surface the C_{60} dimer lattice contracts with respect to the ideal bulk fcc structure while it expands on the (3x3) surface. When more C_{60} s are deposited the resulting triangular or hexagonal C_{60} clusters are therefore under larger stress so that a closed-packing structure cannot be formed. Instead, the second layer C_{60} starts to nucleate on the first layer.

Figure 2: Schematic diagram of the adsorption model for C_{60} on the ($\sqrt{3}\times\sqrt{3}$) and (3x3) surface. (a) The C_{60} adsorbs at the center of the vacancy on the ($\sqrt{3}\times\sqrt{3}$) surface, and forms dimer with the second closest neighbor. The large and small ball are Si and C atom respectively. (b) The C_{60} adsorbs at the top of the (3x3) spots, and form dimer with its nearest neighbor.

3.2 SiC growth

With further coverage increase, the C_{60} formed multiple-layer islands on the two completely filled C_{60} layer on the (3×3) surfaces as shown in Fig. 3(a). The film structure shows the fcc (111) packing with the nearest distance of 10.2 Å. This observation indicates that the film growth on the (3×3) surface is dominated by the van der Waals interaction, suggesting that the C_{60} -substrate interaction is limited up to the first two layer at the interface. On the other hand, on the $(\sqrt{3} \times \sqrt{3})$ phase we did not observe the formation of very ordering structure. Deposition of C_{60} molecules led to the growth of three dimensional clusters, which eventually resulted in the nucleation of large C_{60} islands, suggesting the C_{60} -substrate interaction still influences the multilayer growth of the C_{60} on the $(\sqrt{3} \times \sqrt{3})$ surface.

Annealing the C_{60} film on the Si rich (3×3) surface at 400 °C resulted in the desorption of the C_{60} molecule, except the first layer which showed short range ordering (Fig. 3(b)). After annealing at 850 °C, the C_{60} reacted with the Si to form SiC islands as shown in Fig. 3(c). Further annealing to 1000 °C improved the surface roughness, and resulted in the epitaxial growth of SiC (Fig. 3(d)). Atomically resolved image showed that the surface was $(\sqrt{3} \times \sqrt{3})$ reconstructed. Contrary to the formation of ordered layer structure on the (3×3) surface, annealing the multilayer C_{60} on the $(\sqrt{3} \times \sqrt{3})$ surface did not result in the formation of any ordered structure, and the C_{60} clusters can not be desorbed by annealing to as high as 1050 °C. Only after annealing the surface in a Si flux at 1000 °C the C_{60} molecules reacted with the arriving Si to form SiC, and the surface reconstruction depended on the Si coverage.

Figure 3. (a) STM image of the multilayer fcc(111) C_{60} film formed on the (3×3) surface ($160 \text{ Å} \times 160 \text{ Å}$). (b) The (3×3) surface ($320 \text{ Å} \times 320 \text{ Å}$) after annealing to 400 °C. (c) The SiC islands grown on the (3×3) surface ($480 \text{ Å} \times 480 \text{ Å}$) after annealing to 850 °C. (d) The growth of SiC layer on the (3×3) surface ($1000 \text{ Å} \times 1000 \text{ Å}$) after annealing to 1000 °C.

4. CONCLUSIONS

To summarize, we have studied the C_{60} adsorption on the 6H-SiC(0001) ($\sqrt{3}\times\sqrt{3}$) and (3x3) surfaces by STM. The C_{60} s were found to reside at the center of the honeycomb of the C rich ($\sqrt{3}\times\sqrt{3}$) structure and probably interacted strongly with the Si underneath. While on the Si-rich (3x3) surface they resided on top of the bright protrusions. With increasing coverage, the C_{60} formed clusters of trimers or hexagons on the terraces. The second layer C_{60} started to nucleate on the first layer even without complete the first layer, leaving open space in the first layer. On the (3x3) surface, starting from the third layer C_{60} film of close-packed fcc(111) with close nearest neighboring distance of 10.2 Å was observed. However, on the ($\sqrt{3}\times\sqrt{3}$) surface, the C_{60} continued to grow in three dimensional clusters, which eventually led to large C_{60} islands. The internal structure of the C_{60} molecule consisting of three stripes was also observed on the first and second layer of C_{60} on both surface. The observation was explained by the strain build up in the C_{60} clusters on both surfaces, which limited the growth of the size of the C_{60} cluster. In addition, our observation of the C_{60} adsorption on the ($\sqrt{3}\times\sqrt{3}$) surface provided further support for the vacancy model for this structure. The growth of SiC was also achieved by using C_{60} molecule as carbon source.

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