Carbonization process and SiC formation at C\textsubscript{60}/Si(111) interface studied by SRPES

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Abstract. Carbonization process and SiC formation upon annealing the Si(111) surface covered by C\textsubscript{60} molecules with the thickness of 1.3 nm have been investigated by using synchrotron radiation photoelectron spectroscopy (SRPES), X-ray photoemission (XPS) and reflection high energy electron diffraction (RHEED) in NSRL. C\textsubscript{60} molecules are chemisorbed on the Si(111) surface at room temperature, via Si-C\textsubscript{60} hybridization to form covalent bonds, which can be explained by adsorption model including two adsorption configurations S3 and L. With annealing the sample, the Si-C\textsubscript{60} hybridization weakened C-C bonds internally in C\textsubscript{60} molecules and enhanced the formation of Si\textsubscript{x}C\textsubscript{60}, an intermediate species. Further annealing the sample to 650\textdegree C will lead to the decomposition of C\textsubscript{60} molecules, the released carbon fragment will bond with external silicon atoms to form SiC. While annealing the sample to 850\textdegree C, decomposition of all C\textsubscript{60} molecules was accomplished, and only a SiC film was left on the surface.

1. Introduction
Silicon carbide (SiC) is regarded as a promising material in high power, high frequency and high temperature semiconducting devices, for its wide band gap, high electron mobility, high thermal conductivity, chemical inerterness and hardness\cite{1-2}. Chemical vapor deposition (CVD) has been widely used in growth of SiC films on silicon substrate\cite{3-4}, but growth of high qualitative SiC films needs the substrate to be maintained at a temperature more than 1050\textdegree C, which is a great limit for SiC-based device fabrication. Other substituent methods with low substrate temperature should be developed.

Several groups\cite{5,7,8} have shown that SiC film can be obtained via thermal reaction of C\textsubscript{60} with Si substrate at a temperature as low as 800\textdegree C, obviously lower than that used in CVD. Much has been done to investigate growth methods and morphology of the resulting SiC film\cite{5-9}, knowledge of carbonization process of C\textsubscript{60} with the Si substrate and following formation of SiC film should be payed more attention to. In this paper, we study the annealing behavior of C\textsubscript{60}/Si(111) interface and the following SiC formation by using synchrotron-radiation photoemission experiments.

2. Experimental
All experiments are performed in National Synchrotron Radiation Laboratory (NSRL), Hefei, China. The experimental station is mainly composed of a VG ARUPS10 system. The XPS, LEED, RHEED and AES are also equipped and all these systems work under UHV condition (better than 2 \times 10^{-8} Pa).
The beamline covers the energy range from 10-300eV with energy resolution (E/ΔE) better than 1000. More details of the experimental station and the related beamline are described elsewhere[10].

The sample used in this experiment is a Si(111) single crystal. To obtain a clean surface, the sample is treated chemically using organic solvents and dipped in HF solutions to remove the silicon oxides. Then the sample is blown dry with pure N2 and immediately introduced into the UHV chamber followed by degassing at 500°C for about 3 hours with e-beam heater, then annealing in a stepwise manner to 850°C to remove the protective oxide layers. High purity C60 powder (better than 99.99%) is evaporated via K-cell at 250°C, the pressure is controlled to be less than 1.5×10⁻⁷ Pa during deposition. The evaporation rate is measured by quartz crystal thickness monitor, the total film thickness is about 1.3 nm. The sample covered by 1.3 nm C60 is annealed in a stepwise manner, i.e. from room temperature to 400°C, 600°C, 650°C, 700°C, and 850°C. At each stage the sample is transferred to the analysis chamber for SRPES and XPS measurement to evaluate the chemical reaction process. The sample is cooled down to room temperature (RT) before the measurement. The Si 2p spectra are taken at the photon energy of 150 eV, while C 1s spectra are taken by XPS with Mg Kα for the energy limit of synchrotron radiation source. RHEED measurements are performed in real-time during all stages of the experiment.

3. Results and discussion

![Figure 1 C 1s spectra taken by XPS for various annealing temperatures at the C60/Si(111) interface (C60 thickness 1.3 nm). The sample at RT is displayed in (a). These annealing temperatures are (b) 400°C, (c) 600°C, (d) 650°C, (e) 700°C, (f) 850°C](image)

Figure 1 shows the evolution of C 1s spectra taken by XPS upon annealing the sample at different temperatures. All spectra are decomposed by a least square fitting procedure, the background is subtracted by the Shirley method[11]. Fig.1 (a) displays the spectrum taken at RT, where two peaks A and D are observed with an analytical fit. The binding energy of peak A is 284.33 eV, coincides with that of C 1s from C60 molecule solid[12]. Peak A should originate from C atoms in C60 cage. Peak D is at binding energy of 283.33 eV with wide FWHM, nearly 1 eV lower than peak A, which suggests that electrons move from the Si substrate to adsorbed C60 molecules. It means that C60 molecules hybridize with external silicon atoms, and C60-Si bonds are formed. Upon annealing, the intensity of peak A decreases but its binding energy almost keeps the same; the intensity of peak D increases and reaches the maximum at 650°C, while with temperature increasing its binding energy shifts gradually towards...
lower. It obviously means that annealing leads to the increase of numbers of C\textsubscript{60}-Si bonds, and more electrons move from the Si substrate to adsorbed C\textsubscript{60} molecules. When the temperature reaches 650°C, a new peak E located at 282.6 eV starts to develop; further annealing to higher temperature, its intensity increases fast while peak D decreases greatly. When annealing to 850°C, peak E becomes the only one feature in C 1s spectra. Its binding energy is at 282.8 eV, which agrees well with that of crystalline SiC\textsuperscript{[13-14]}. This phenomena shows that at 650°C SiC starts to form at the interface. While at 850°C all the adsorbed C\textsubscript{60} molecules decompose and react with the silicon substrate, only SiC film is left on the surface.

Figure 2 shows the Si 2p spectra taken at the photon energy of 150 eV upon annealing at different temperatures. All spectra are normalized and decomposed by a least square fitting procedure. The spin-orbit splitting of Si 2p is 600 ± 10 meV, the branching ratio is 0.50 ± 0.01. The background is subtracted by the Shirley method. As shown in Fig.2 (a), deposition of C\textsubscript{60} induces two components, C\textsubscript{1} and C\textsubscript{2}. The energy difference between the bulk component (B) and C\textsubscript{60}-induced components (C\textsubscript{1} and C\textsubscript{2}) is 1.03 eV and 0.31 eV respectively. This can be explained by adsorption model proposed by Daniel\textsuperscript{[15]}. Both C\textsubscript{1} and C\textsubscript{2} components can be attributed to different adsorption configurations. C\textsubscript{1} component is attributed to L adsorption configuration, where there are five Si-C bonds between C\textsubscript{60} molecule and external Si atoms; C\textsubscript{2} component is attributed to S3 adsorption configuration, where there are three Si-C bonds between C\textsubscript{60} molecule and external Si atoms. All these agree with former experimental work\textsuperscript{[16-18]}, where they stated these two components can be attributed to covalent Si-C\textsubscript{60} bonds, labeled as Si\textsubscript{6}C\textsubscript{60}.

Upon annealing the sample to 600°C, bulk component (B) persists in attenuation while the intensities of C\textsubscript{1} and C\textsubscript{2} components increase, which consists well with the increase of D component in C 1s spectra. Further annealing to 650°C, C2 component keeps on increasing, while C1 component is replaced by a new component F whose binding energy is more closer to that of SiC. F component can be believed to be a combination of C1 component and component of SiC. It means that at 650°C some C\textsubscript{60} molecules related with C1 component start to decompose and form SiC at the interface.
When the temperature reaches 700°C, the intensity of C2 component starts to attenuate, while both of bulk component and F component show a strong increase. It shows that further annealing to higher temperature as 700°C will lead C atoms which are related with C2 component also start to form SiC. After the temperature reaches 850°C, only F component and bulk component (B) can be observed in the spectra, where bulk component (B) takes the main part. Here the binding energy of F component is 100.25 eV, which agrees well with that of SiC. All these support the results concluded from C 1s spectra. It is obvious that at 650°C the C_{60}/Si interface undergoes some changes. Below 650°C, nearly all C_{60} cages are preserved; but above 650°C, C_{60} cages begin to decompose and SiC starts to form. At 850°C the surface is no longer covered by thick C_{60} molecules, but is covered by thin SiC film. So the Si 2p signals taken from the Si substrate with thin SiC film as shown in Fig.2(f) are more than that taken from the Si substrate covered by C_{60} at RT as shown in Fig.2(a).

RHEED patterns taken during some stages of the experiment are showed in Figure 3. All these RHEED patterns are displayed as negative image for clarity. Fig.3 (a) shows the pattern of the clean Si(111) surface before C_{60} evaporation. Note that the RHEED pattern is clearly streaky and shows the presence of the Kikuchi lines, which suggests a clean and smooth surface of Si substrate. After annealing the sample to 650°C, the stripes related with clean Si(111) surface almost disappear in the pattern as shown in Fig.3 (b). With careful observation, we can find the appearance of some new but very faint streaks outside the original streaks. Further annealing the sample to 850°C as shown in Fig.3 (c), the new streaks increase to be more clear and visible, which are different from the original streaks in Fig.3 (a). The stripe spacing is proportional to the inverse lattice spacing of the surface. The ratio of the new streak spacing to the original one agrees well with the ratio of the inverse lattice spacing of SiC to that of Si. It is obvious that the patterns in Fig.3 (c) belong to SiC. From the results of RHEED patterns, it shows that at 650°C SiC starts to form and at 850°C the surface is covered by SiC film, which confirms the former results obtained from photoemission.

4. Conclusion
We have demonstrated a detailed carbonization and SiC formation process for C_{60}/Si interface upon annealing. At room temperature, C_{60} molecules are chemisorbed on the Si(111) surface via Si-C_{60} hybridization. With annealing the sample, the Si-C_{60} hybridization weakens C-C bonds internally in C_{60} molecules and enhances the formation of Si_{x}C_{60}, an intermediate species. At 650°C, C_{60} molecules start to decompose, the decomposition releases fragmented carbon to bond with Si atoms to form SiC. Upon further annealing to 850°C, all C_{60} molecules decompose, only SiC film is left on the surface.

Acknowledgement
This work is supported by National Natural Science foundation of China (No.50572100).
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