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Thermally induced decomposition of single-wall carbon nanotubes adsorbed on H/Si(111)

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The thermally driven reaction of carbon nanotubes with a silicon substrate is studied by photoemission spectroscopy and atomic force microscopy. Carbon nanotubes with a relatively high defect density are observed to decompose under reaction with silicon to form silicon carbide at temperatures (650 ± 10 °C) substantially lower than the analogous reaction for adsorbed C_{60} . The morphology of the resultant silicon carbide islands appears to reflect the morphology of the original nanotubes, suggesting a means by which SiC nanostructures may be produced. © 2002 American Institute of Physics. [DOI: 10.1063/1.1530747]

Understanding the interaction of carbon nanotubes with silicon and the resultant formation of silicon carbide at elevated temperatures is of importance due to the need to create well-defined nanotube/semiconductor heterojunctions¹ and the growing interest in fabricating silicon carbide nanorods from carbon nanotube precursors.^{2–4} Moreover, knowledge of the temperature at which carbide formation occurs is necessary to determine the stability of silicon/carbon nanotube interfaces which would result from integration of carbon nanotubes with silicon-based electronics. Although much effort has been directed toward understanding the interaction and thermal decomposition of C_{60} on Si(111) surfaces,^{5–11} a closely related system, the inability to evaporate carbon nanotubes makes exploring the interaction of these species with elemental surfaces difficult.

In this letter, we report an approach in which nanotubes are deposited on hydrogen passivated Si(111) surfaces in an ambient atmosphere. Hydrogen is subsequently desorbed from beneath the nanotubes in an ultrahigh vacuum (UHV) environment allowing the study of the nanotube/silicon interface as a function of temperature by photoemission spectroscopy. Desorption of hydrogen from Si(100)- 2×1 -H has previously been observed to occur beneath a C_{60} monolayer enabling molecules to bond directly to the silicon surface.¹² We find that defective carbon nanotubes decompose on Si(111) after a short anneal at 650 ± 10 °C, about 150 °C (Refs. 6–10) lower than the decomposition temperature of C_{60} on Si(111)- 7×7 . *Ex situ* atomic force microscopy (AFM) indicates that the morphology of silicon carbide islands re-

sulting from nanotube decomposition is governed by initial nanotube geometry, suggesting a route for fabrication of nanometer scale silicon carbide structures.

Photoemission experiments were undertaken at Beamline 4.1 of the Synchrotron Radiation Source, Daresbury, UK. Hydrogen passivated Si(111) substrates were produced by conventional techniques and AFM images show large flat terraces, while x-ray photoelectron spectroscopy (XPS) demonstrated very low levels of residual oxide contamination. Purified single-wall carbon nanotubes (SWNTs) were supplied by the Sussex Fullerene Group and were placed in suspension by agitating small quantities in acetone in a conventional ultrasonic bath. Several droplets of the sol were cast upon a hydrogen passivated Si(111) sample, and the sample was immediately placed in the load lock of a UHV chamber. After pumping, the samples were transferred to the UHV chamber (base pressure: 8×10^{-11} mbar) for photoemission measurements. Spectra were obtained in angle integrating mode using a Scienta SES-200 electron analyzer and synchrotron radiation for valence band spectra ($h\nu=40$ eV), or a conventional x-ray gun (Mg $K\alpha$, $h\nu=1253.6$ eV) for core-level measurements. Binding energies in valence band spectra are referred to the Fermi level of a Ta plate in electrical contact with the sample. XPS binding energies were calibrated against a Pt foil and checked for consistency with the binding energy of the Si $2p$ line. Typical resolution was 0.125 eV for valence band spectra and 0.85 eV for XPS. Annealing was performed by passing a current directly through the sample, with the sample temperature measured using an optical pyrometer. The sample was held for 5 min at each annealing temperature, before being allowed to cool to room temperature for measurement.

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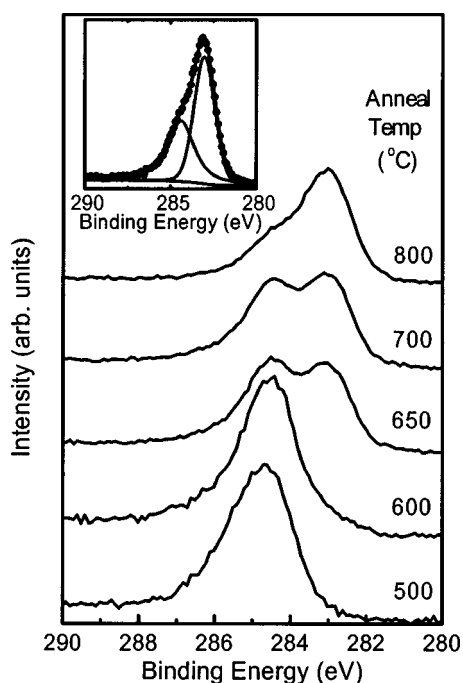


FIG. 1. C 1s spectra as a function of annealing temperature for SWNTs deposited on hydrogen passivated Si(111) showing decomposition of the nanotubes and SiC formation. The inset shows a two-component fit to the C 1s spectrum obtained after 30 min annealing at 800 °C.

The evolution of C 1s spectra as a function of annealing a clean SWNT film is shown in Fig. 1. An initial anneal to 500 ± 10 °C is employed to remove contamination from the ambient atmosphere and residual solvent, and to desorb H from the substrate. The resulting C 1s line is centered at 284.6 ± 0.1 eV consistent with previous photoemission studies of SWNTs.^{13,14} Annealing to 600 ± 10 °C does not provoke a significant change in C 1s line shape, however, at a temperature of 650 ± 10 °C, a second component at lower binding energy is clearly visible. A two-component fit to the spectra¹⁵ with a Shirley background (a typical fit is shown in the inset of Fig. 1) shows that the new C 1s component has a binding energy of 283.0 ± 0.1 eV. This value, and associated shakeup feature (not shown), are consistent with SiC,¹⁶ thus we assign the new peak to SiC formed by the thermally induced decomposition of SWNTs. As the annealing temperature is increased to 800 ± 10 °C, the SiC peak increases at the expense of the SWNT peak demonstrating that further nanotube decomposition occurs with increasing temperature. In addition, the SWNT peak shifts gradually to a binding energy of 284.4 ± 0.1 eV. Further annealing at 800 ± 10 °C for periods of up to 30 min leads to no significant further change. If we assume that the area under the SWNT and the SiC components of the C 1s line are proportional to the amount of carbon in each state, a fit to the C 1s line shape obtained after a 30 min anneal at 800 ± 10 °C (Fig. 1, inset) indicates $\sim 40\%$ of the carbon remains in the form of nanotubes even after a lengthy anneal. The lack of complete reaction between the SWNTs and the silicon at 800 °C can be explained by the relatively low diffusion rate for Si through SiC.^{1,5} The outermost nanotubes in an aggregate or bundle will react readily with the silicon forming a SiC layer around the nanotubes deeper within, preventing silicon from reaching the inner nanotubes at modest annealing temperatures.



FIG. 2. AFM image ($1 \mu\text{m} \times 0.69 \mu\text{m}$) of an annealed (800 °C) SWNT/H-Si(111) sample. The morphology of the clusterlike islands is similar to that of as-deposited SWNT aggregates.

The morphology of samples annealed to 800 ± 10 °C was revealed by *ex situ* AFM performed under ambient conditions. A low density of clusterlike islands similar to, but smaller and much more sparse than, those observed by AFM after decomposition of a C₆₀ monolayer on Si(111)-7×7 (Ref. 7) could be seen across the sample. In addition, we frequently observed aggregates of larger clusters, from which linear arrays could often be seen to radiate, as shown in Fig. 2. Excluding the obvious granularity seen in the images, the overall morphology is reminiscent of that observed for as-deposited SWNTs (not shown) in which individual nanotubes or bundles radiate from larger aggregations. Therefore, we suggest that the clusters are formed by a reaction between SWNTs, or SWNT bundles, and the silicon substrate, and that the distribution of SiC grains reflect the geometry of the original carbon nanotubes. Hence, it may be possible in the future to create SiC nanostructures by the reaction of SWNTs placed at selected locations and the silicon substrate on which they are supported.

The C 1s spectra indicate that a significant decomposition of SWNTs occurs at temperatures as low as 650 ± 10 °C, ~ 150 °C below that at which C₆₀ is observed to form SiC.^{6–10} The lower temperature at which SWNT decomposition occurs at first appears anomalous—curvature of carbon nanotubes and associated bond strain is smaller than in fullerenes and, in the absence of defects, there are no five-membered rings, suggesting that carbon nanotubes should be theoretically more stable. However, valence band photoemission spectra [Fig. 3(a)] demonstrate that graphitization in the SWNTs studied is far from complete. Valence band spectra from the SWNTs used in this study, obtained from clean samples prior to SiC formation [Fig. 3(a)], are similar to those measured, using a similar photon energy, on amorphous carbon (*a*-C) samples with a relatively large diamondlike *sp*³ to a graphitelike *sp*² bonding ratio.¹⁷ In comparison, spectra obtained from clean (annealed to 500 °C) thick films of purified commercial HiPco SWNTs [Fig. 3(b)] bear strong resemblance to *a*-C annealed to a high temperature,¹⁷ in which a negligible degree of *sp*³ bonding remains. The presence of significant *sp*³ bonding in the SWNTs used in the annealing experiments indicates a relatively high defect density, which explains why they react with a silicon substrate more readily than C₆₀ despite theoretically greater stability.

In summary, we observe that SWNTs adsorbed on pas-

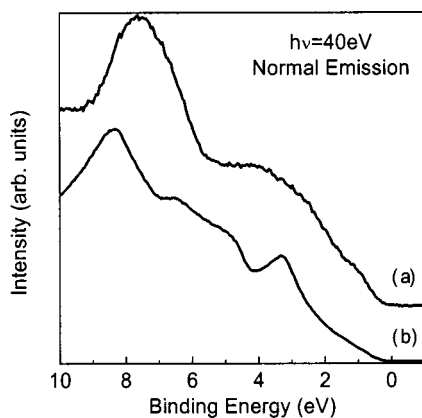


FIG. 3. Valence band spectra (obtained with 40 eV photon energy) of (a) a thin film of SWNTs as used in the annealing experiments and (b) a thick film of purified HiPco SWNTs.

sivated Si(111) decompose to form surface SiC upon annealing, due to hydrogen desorption and subsequent reaction with the silicon surface. The temperature at which decomposition takes place appears strongly influenced by defect density in the nanotubes—the rather defective SWNTs used in this study were found to decompose at lower temperature than theoretically less stable C_{60} . The morphology of the SiC islands formed by the reaction between the SWNTs and silicon surface appears to reflect the morphology of the original nanotubes suggesting a means by which SiC nanostructures may be fabricated.

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