Growth and Characterization of Graphene on Silicon Carbide

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Abstract:

Epitaxial graphene layers were fabricated by thermal decomposition of silicon (Si)-terminated ^{4}H-SiC(0001) in ultrahigh vacuum (UHV) at different temperatures. Raman spectra and Auger electron spectra show that graphene layers can form after annealing at 1300°C, and a heating recipe should be optimized between 1300°C and 1400°C. Scanning tunneling microscope (STM) images reveal Moiré patterns in our multi-layer graphene providing evidence of a rotated phase in which individual layers are electronically decoupled.

Introduction:

Graphene, a single monolayer of sp^2-bonded carbon atoms, has recently attracted much attention due to its novel quantum electrodynamic properties [1] and the potential of carbon-based electronics [2]. Due to a linear dispersion of energy at the constant (κ)-point, graphene's charge carriers behave as fermions with zero rest mass and mimic relativistic particles described by the Dirac equation. Graphene is a zero-gap semiconductor with charge carriers that travel ballistically through the two-dimensional material and is stable under ambient conditions [3]. However, large-scale growth of high quality graphene for both bench-top experiments and carbon-based device engineering presents a challenge. Mechanical exfoliation of HOPG produces the highest quality graphene but is not scalable [2]. Other growth methods include chemical vapor deposition [4], surface segregation of carbon doped metals [5], and thermal decomposition of silicon carbide (SiC) [6]. The latter is attractive because SiC can be integrated into silicon technology. Additionally, multi-layer graphene grown on the carbon face of ^{4}H-SiC has been shown to retain the electrical properties of a single sheet of graphene as adjacent layers are rotated and electronically decoupled [7]. Here we present preliminary work optimizing a heating procedure for graphene growth via thermal decomposition of Si-terminated ^{4}H-SiC(0001) as well as evidence that multi-layer graphene grown by our method exists as a rotated phase and may behave like a single sheet of graphene.

Experimental Procedure:

^{4}H-SiC(0001) samples roughly 1 mm × 8 mm in size were cut using a diamond scribe and cleaned ultrasonically with ethanol and acetone. The samples were heated individually in a UHV (base pressure 10^{-11} mbar) preparation chamber. At high temperature, silicon atoms sublimate from the SiC surface and the remaining carbon atoms are left to rearrange and form graphene. Samples were heated at intervals between 1150°C and 1600°C for different lengths of time. STM and atomic force microscopy (AFM) measurements were taken at room temperature in UHV. Electrochemically etched tungsten STM probes were argon sputtered for 15 minutes and used throughout. *In situ* field evaporation was used to further clean the tip apex. AES measurements were performed at room temperature with a scanning Auger microscope (ULVAC-PHI model SAM680) with a cylindrical mirror analyzer. AES spectra were recorded with a primary electron beam of 10.0 kV. Differential dN(E)/dE Auger spectra were obtained by numerical derivation of raw N(E) integrated Auger data by Savitzky-Golay differential filter using five points. Raman spectra were recorded by Raman microscope (JY-6400) at room temperature. The Ar ion laser of 532 nm was used as the excitation source with the laser power 100 mW.

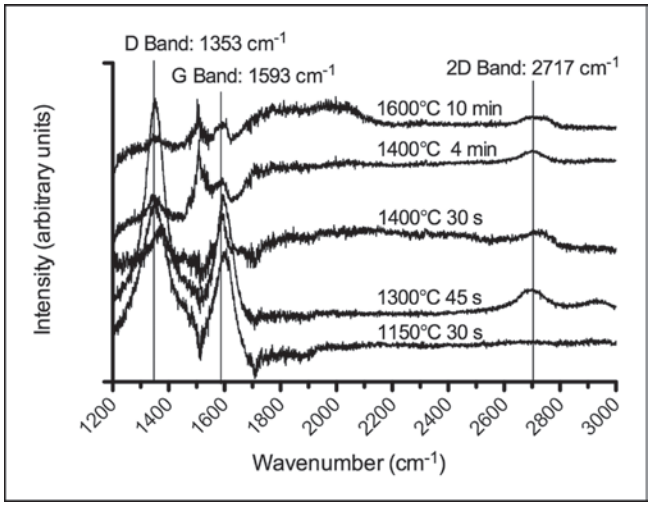

Figure 1: Normalized Raman spectra of five samples corrected by subtracting the substrate (SiC) spectra.

Results and Discussion:

Figure 1 shows the Raman spectra for ^{4}H-SiC(0001) surfaces after annealing at different temperatures. Three distinct peaks in the Raman spectra are characteristic of graphene: the defect-induced D band (~ 1353 cm^{-1}), the in-plane vibrational G band (~ 1593 cm^{-1}), and the two-phonon 2D band (~ 2717 cm^{-1}) [8].

Each of these peaks was clearly visible in all our samples with the exception of the 2D band in the 1150°C sample (Figure 1). This indicated that 1150°C was not sufficiently high a temperature for graphene growth. The defect-induced D band peak at 1353 cm^{-1} was very strong in the spectra of samples grown below 1400°C. This indicated that edge state characteristics dominated in samples heated below 1400°C because of small grapheme domains. Above 1400°C the spectra showed undesirable features. We concluded from this Raman analysis that 1400°C for a short time was a good temperature around which to optimize the heating procedure.

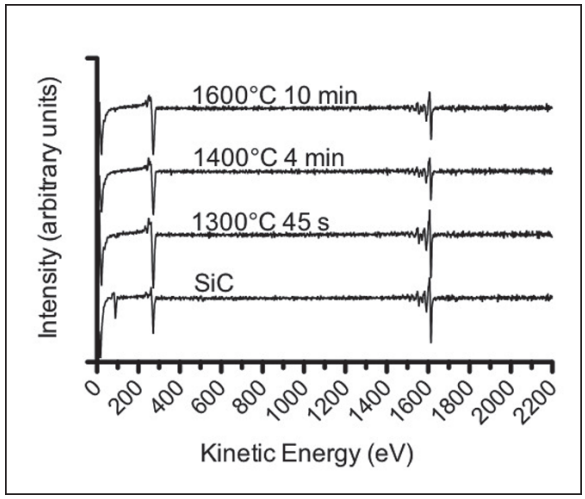

Figure 2: Differential Auger spectra for three samples and substrate.

Auger electron spectroscopy provided additional macro-scopic information about the surface. Figure 2 shows the differential Auger spectra for four samples annealed at different temperatures and the SiC surface. The spectra were characterized by three peaks: a low-energy Si LVV peak at 84 eV, a high energy Si KLL peak at 1610 eV, and a C KLL peak at 265 eV. The mean free paths of the Si LVV and the Si KLL peaks were approximately 0.5 and 2.4 to 3.0 nm respectively [9]. We concluded from the decreased Si LVV peak intensity that at 1300°C the carbon concentration had already increased on the surface and optimization of a heating procedure should begin around this temperature. The increase in background noise of the Si KLL peak as well as the relative C KLL and Si KLL peak intensities indicated increased carbon concentration at higher temperatures, as we expected.

STM images from as-received SiC following graphitization at 1400°C for 1 minute are shown in Figures 3 and 4. Individual graphene layers and islands are distinguishable in Figure 3. There were a large number of defects including carbon nanotubes which were found growing simultaneous with graphene layers. Figure 4 shows an atomic resolution image with a Moiré pattern which indicated that the top layer of graphene was rotated with respect to the layer below it; evidence that individual layers were electronically decoupled.

Future Work:

A heating recipe for graphene on ^{4}H-SiC(0001) should be optimized between 1300°C and 1400°C. A pre-heating hydrogen-etch to remove scratches from commercial polishing may be necessary. STM images should be taken at regular temperature intervals to establish a better understanding of the growth mechanism.

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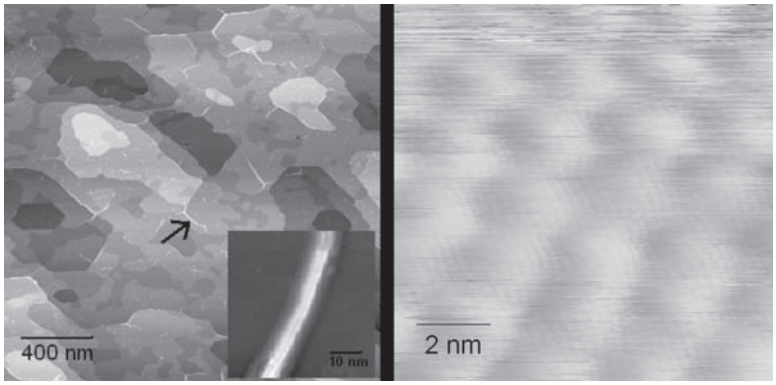

Figure 3, left: STM image of sample heated to 1400°C for one minute. Features similar to the one indicated by arrow are carbon nanotubes. Inset: UHV AFM image of a bundle of carbon nanotubes.

Figure 4, right: STM image of sample heated to 1400°C for one minute. The Moiré pattern is evident.