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Graphene on Carbon-face SiC{0001} Surfaces Formed in a Disilane Environment

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Abstract. The formation of epitaxial graphene on SiC(000 $\bar{1}$) in a disilane environment is studied. The higher graphitization temperature required, compared to formation in vacuum, results in improved thickness uniformity of the graphene films. Some areas of the surface display unique electron reflectivity curves not seen in vacuum-prepared samples. Using selected area diffraction, these areas are found to have a graphene/SiC interface structure with a graphene-like buffer layer [analogous to what occurs on SiC(0001) surfaces].

Introduction

Epitaxial graphene on SiC{0001} has been intensively studied over the past five years as a potential means of producing *large area* graphene for electronic applications [1]. There are two inequivalent faces of SiC{0001} – the (0001) face, also known as the Si-face, and the (000 $\bar{1}$) face or C-face. On both surfaces graphene can be formed by heating the SiC in vacuum, causing preferential sublimation of the Si atoms thereby leaving behind an excess of C atoms which self-assembles into graphene. Preparation is also possible in other environments including argon [2-4], or disilane [5]. The advantage of using these environments is that they permit independent control of the sample temperature and the Si partial pressure during the graphene formation, thus enabling a reduction in Si sublimation rate (at a given temperature) so that a higher formation temperature can be used, hence, improving the graphene quality.

The prior work involving graphene formation in argon has been most successful for the Si-face [2-4]. In fact, for the C-face, improvement in structural properties using an argon environment was *not* obtained, particularly for thin, monolayer (ML) graphene films [6,7]. The reason for this lack of success on the C-face occurs, we believe, is unintentional oxidation of the C-face surface in the presence of the Ar background [7]. With the goal of achieving uniform, thin graphene layers on the C-face, we have studied the graphene formation in a disilane environment. For disilane pressures around 10^{-5} Torr we find modest improvement in the graphene structural properties compared to vacuum formation. At higher pressure near 10^{-4} Torr, we obtain considerably better uniformity in the graphene thickness for thin \approx ML-thick films. We also find the presence of a new graphene structure on the surface compared to that observed in vacuum-prepared samples, which we identify as a *graphene-like buffer layer* bonded to the SiC, analogous to the $6\sqrt{3}\times 6\sqrt{3}$ -R30° (denoted $6\sqrt{3}$ for short) layer that acts as a buffer on the Si-face [8,9].

Experimental

Experiments are performed on nominally on-axis, n-type 6H-SiC or semi-insulating 4H-SiC wafers purchased from Cree, Inc., with no apparent differences between results for the two types of wafers. These wafers are cut into 1×1 cm² samples. Prior to graphene formation, the samples are cleaned in 5×10^{-5} Torr of disilane by heating to 850°C for 5 min, which is found to remove polishing damage in a similar manner as for H-etching [10]. To form the graphene, the samples are then heated in 10^{-6} – 10^{-4} Torr of disilane at 1200 - 1400°C for 10 to 30 min. Temperature is measured using a disappearing filament pyrometer [10]. Low-energy electron microscopy (LEEM) and diffraction

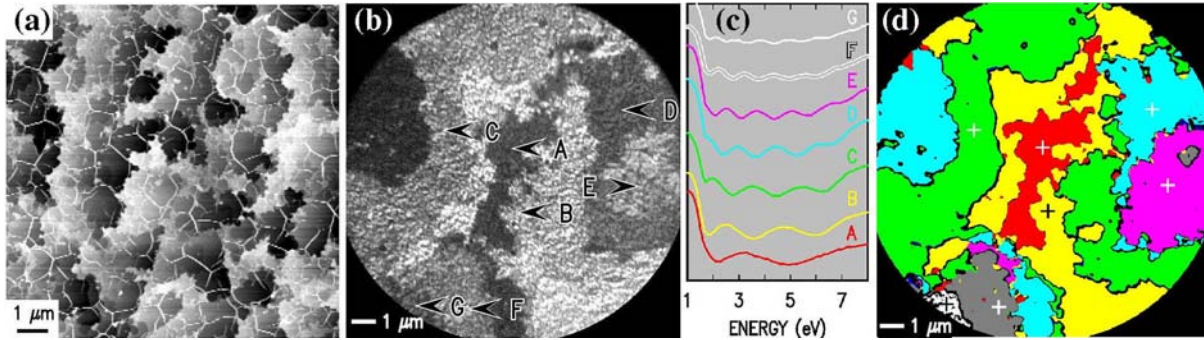


FIG 1. Results for graphene on the C-face prepared by annealing in 1×10^{-6} Torr of disilane at 1290°C for 15 min. (a) AFM image, displayed using gray scale range of 4 nm. (b) LEEM image acquired at electron beam energy of 2.3 eV. (c) Intensity of reflected electrons from the points marked in (b), as a function of electron beam energy. Curves A – G correspond to 2 – 8 ML of graphene, respectively. (d) Map of local graphene thickness, using the same shades as in (c). Small white or black crosses mark the same locations as in (b).

(LEED) are performed in an Elmitec LEEM III system. During LEEM, the sample and the electron gun are kept at a potential of -20 kV and LEEM images are acquired with electrons having energy, set by varying the bias on the sample, in the range of 0-10 eV. The intensity of the reflected electrons from different regions of the sample is plotted as a function of the beam energy, with the number of graphene MLs given by the number of local minima in the reflectivity curve [11]. From sequences of images acquired at energies varying by 0.1 eV, color-coded maps of the graphene thickness are generated using the method described in Ref. [4]. Surface morphology is measured in air by atomic force microscopy (AFM), using a Digital Instruments Nanoscope III in tapping mode.

Results

Results for graphene formation on the C-face at a disilane pressure of 1×10^{-6} Torr are shown in Fig. 1. The AFM image of Fig. 1(a) shows the surface morphology, whereas the LEEM results of Figs. 1(b) and 1(c) can be analyzed to produce a map of the local graphene thickness, Fig. 1(d). At this relatively low disilane pressure, there is a modest improvement in structural homogeneity compared to vacuum formation, similar to the situation found for Si-face graphene formed under low or high ($10^{-6} - 10^{-4}$ Torr) disilane pressure [12]. The annealing temperature used for the sample of Fig. 1 is about 100°C higher than for a film with the same average thickness (4.2 ML) formed in vacuum, so this modest improvement in quality is expected. This graphene film displays a considerable range of thicknesses, similar to that found for vacuum preparation [7]. However, one notable difference between the results of Fig. 1 compared to our vacuum-prepared C-face graphene [7] is the network of raised (white) lines prominently seen in Fig. 1(a). These ridges arise from the different thermal expansion coefficients between the graphene and the SiC. As emphasized by Hass et al., the presence of such features is an indicator of a structurally ideal graphene film [1].

Results for a C-face film prepared under a higher pressure of disilane, 5×10^{-5} Torr, are shown in Fig. 2. A thinner film was formed in this case as compared with Fig. 1. The surface morphology measured by AFM, shown in Fig. 2(a), displays islands of graphene as revealed again by the presence of the raised (white) lines on the surface, surrounded by featureless areas that apparently contain no graphene. The electron reflectivity curves in Fig. 2(c) contain a number of new features compared to those in Fig. 1(c). Considering first the curves B, C, and D of Fig. 2(c), they contain 1, 1, or 2 minima in the reflectivity over the energy range 2.0 – 6.2 eV, as expected for 1, 1, or 2 ML of graphene, respectively, but curve B also contains a new minimum near 6.8 eV. This new feature is even more intense at surface areas that display a reflectivity curve completely different than those associated with graphene layers, as seen in curve A of Fig. 2(c).

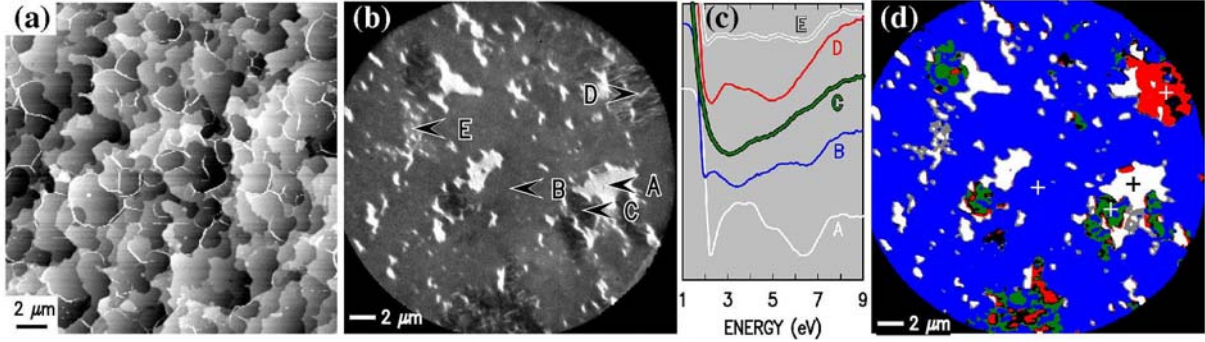


FIG 2. Results for graphene on the C-face prepared by annealing in 5×10^{-5} Torr of disilane at 1270°C for 15 min. (a) AFM image displayed using gray scale range of 3 nm. (b) LEEM image acquired at electron beam energy of 3.2 eV. (c) Intensity of reflected electrons from the points marked in (b), as a function of electron beam energy. Curve A corresponds to the oxidized buffer layer, B to 1 ML of graphene on that oxidized buffer, C to a ML of graphene on a non-oxidized buffer, D to 2 ML of graphene on non-oxidized buffer, and E to an ill-defined region. (d) Map of local graphene thickness, using the same shades as in (c). Small white or black crosses mark the same locations as in (b).

We associate this new reflectivity curve A of Fig. 2(c) with a graphene-like layer in contact with the SiC, i.e. the base or "buffer" layer of graphene. There are several reasons for this identification: (i) this curve appears only on samples with very thin (sub-ML) films of graphene films, consistent with it being the layer nearest the SiC, (ii) the reflectivity curve itself resembles that found for the $6\sqrt{3}$ buffer layer found on the Si-face of SiC [11], albeit with the extra minimum near 6.3 eV which we explain below is associated with oxidation of the underlying SiC, (iii) the reflectivity minimum near 6.3 eV also appears in the curve of some overlying graphene, i.e. curves B of Fig. 2(c) [albeit shifted up to 6.8 eV], consistent with our identification of this layer being the base layer, and (iv) electron diffraction of this layer reveals spots identical with those found on the overlying graphene layer, as further discussed below, demonstrating that this base layer does indeed have the graphene structure [13]. Regarding curve E of Fig. 2(c), this curve appears to arise from a combination of areas with characteristics as in curves A – D.

Broad-area low-energy electron diffraction (LEED) patterns of the sample of Fig. 2 reveal a $\sqrt{3} \times \sqrt{3}$ -R30° arrangement of spots in addition to the usual graphene streaks, as shown in Ref. [13], and an intensity vs. energy analysis of those spots reveals that the SiC is covered with the well known silicate layer [14]. Those patterns were, however, acquired *ex situ* after the sample had been exposed to air for several days or more. LEED patterns acquired *in situ* immediately following the graphene formation still reveal the graphene streaks, but instead of the $\sqrt{3} \times \sqrt{3}$ -R30° silicate pattern they show a complex pattern of satellite spots around the main SiC spots, somewhat similar to the $6\sqrt{3} \times 6\sqrt{3}$ -R30° pattern seen for the Si-face buffer layer [9]. These observations are consistent with our identification of the base graphene layer in the samples of Fig. 2 being an oxidized graphene-like buffer layer. The effect of the oxidation is to decouple the buffer layer from the SiC (hence making it into the first graphene layer), as previously observed on the Si-face using either hydrogenation [15] or oxidation [16]. Selected-area LEED patterns acquired from the sample of Fig. 2, after air exposure, reveal spots with precisely the graphene wavevector at *all* points over the surface, i.e. in particular for the areas in Fig. 2 displaying reflectivity curves like that of curve A in Fig. 2(b) [13]. This observation of the graphene structure for those areas confirms our identification of their structure as being a graphene-like buffer layer.

For vacuum-prepared graphene on the C-face, 2×2 and 3×3 LEED patterns are commonly observed, and we observe the same in our work [12]. These arrangements are found to persist at the graphene/SiC interface [17], and their presence has been associated with a weakly-bonded graphene layer on the SiC [9]. In contrast, the C-face buffer layer we observe here corresponds to a strongly-bonded graphene layer on the SiC, and indeed, this type of bonding arrangement was observed in

one prior study [18]. We conclude that the structure of the interface between graphene and C-face SiC depends on the preparation conditions for the graphene. The buffer-layer structure found here is analogous to what occurs for Si-face SiC, and it likely provides a template for the formation of the graphene layers. Control of this interface structure thus provides a route for improved graphene formation on C-face SiC.

Summary

Graphitization of the C-face of SiC in a background of disilane leads to thinner and more uniform films as the pressure of the disilane is increased. Some regions show unique reflectivity curves in LEEM which we identify as a graphene-like buffer layer with the underlying SiC being oxidized.

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