Influence of the silicon carbide surface morphology on the epitaxial graphene formation

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Graphene grown on SiC(0001) by Si depletion has a stepped surface with terraces and step heights up to 10 times larger than those observed in the original SiC surface. This is due to an additional step bunching that usually occurs during graphene formation. In this work, we show that such process can be suppressed by controlling the initial step structure of the SiC surface. In this case, the graphene monolayer is formed on the SiC without modification of the original surface morphology. We observe that the absence of step bunching during growth has no influence on the graphene structural quality. © *2011 American Institute of Physics*. [doi:10.1063/1.3638058]

Graphene has been shown to be a very interesting material for fundamental investigations, revealing singular physical properties.[1–3] Due to some of these properties, particularly those related to electronic transport,[2,3] this material has also been considered as a promising candidate for future electronic applications. Motivated by such scientific and technological interests, the research on the synthesis of high quality graphene by different methods has been intensified in the last few years.[4–8] However, regarding industrial applications, only few of the utilized techniques appear as viable routes to produce graphene on a large scale, namely chemical vapor deposition (CVD) on catalytic metal surfaces,[4,9] and epitaxial graphene (EG) grown on silicon carbide (SiC) by surface thermal decomposition.[8,10–12] The latter approach is particularly attractive since the graphene sheets can be formed directly on an insulating SiC wafer, which enables subsequent device processing and electronic characterization without the need of transferring the graphene layers to another insulating template. Graphene layers can be produced on both (0001) and (000-1) hexagonal SiC polar faces. Even though multilayer graphene films on SiC(000-1) face, due to the rotational disorder between them, behave electronically very similar to free-standing single layer graphene (e.g., offering high charge carrier mobility),[11] a close control over the number of grown layers on this face is difficult.[13] On the other hand, despite its stronger interaction with the substrate, the epitaxial growth of single layer graphene on the SiC(0001) face is easily achieved. Moreover, by using specific strategies such as hydrogen intercalation,[14] excellent mobilities can also be measured for EG on this crystal face.[15]

The growth kinetics of EG on SiC has been extensively investigated.[16–19] In particular, the stepped SiC surface, which occurs due to the miscut of the SiC wafers, has been shown to be crucial for the preparation of high quality layers. Several investigations indicate that the step edges act as nucleation centers for the graphene formation, as in this region the Si and C atoms are weakly bonded.[16–19] To obtain the stepped surface, it is necessary to etch the substrate at high temperatures in a hydrogen atmosphere. This procedure not only leads to step formation on the surface (usually 1.5 nm high) but also removes surfaces irregularities such as scratches resulting from the polishing process. The final graphene layer that is formed by thermally treating the H-etched SiC surface also has a stepped morphology. However, in this case the steps are about 5-15 nm high and the terraces show widths of about 3 μm.[10] The difference in the step dimensions before and after graphene growth is due to an additional step bunching which occurs during the graphene formation. Since this step bunching has been observed in all previous investigations, it is not clear if it is essential for the formation of high quality graphene. In this letter we investigate the formation of epitaxial graphene on stepped SiC(0001) surfaces having different surface morphologies obtained by H-etching as a function of the temperature. We show that the step bunching during EG formation can be suppressed with no changes in the graphene structural quality and morphology. This reveals that the additional step bunching during graphene growth is not a prerequisite for high quality graphene formation. Moreover, the results suggest that graphene can be grown on SiC surfaces with a given pre-defined step structure.

The EG samples used in this work were prepared on 6H-SiC(0001) substrates with dimensions of 1×1 cm^2. The substrates were cut from a nominally on-axis 2 inch *n*-type wafer polished on the (0001) face (epi-ready process by NovaSiC). They were chemically cleaned in n-butyl-acetate, acetone, and methanol. The following processing steps, namely the H-etching and graphene growth, were both performed in a furnace equipped with an induction heating system. In order to obtain SiC samples offering surfaces with different step heights and terrace widths, the H-etching treatments were carried out at different temperatures (ranging from 1350 °C up to 1550 °C) for 15 min in a forming gas atmosphere (95 at.% Ar and 5 at.% H) of 900 mbar and a flow rate of 500 sccm. Finally, EG was prepared on all SiC surfaces (including a non-etched one) at 1600 °C in a 900 mbar Ar atmosphere, as proposed by Emtsev *et al.*[10]

The surface morphology of the samples before and after the EG preparation was investigated by means of atomic force microscopy (AFM) measurements. The image depicted in Fig. 1(a) corresponds to the surface of a non-etched sample, which is composed of steps with a height of ~0.3 nm and terraces with a width of ~0.2 μm. Fig. 1(b) illustrates

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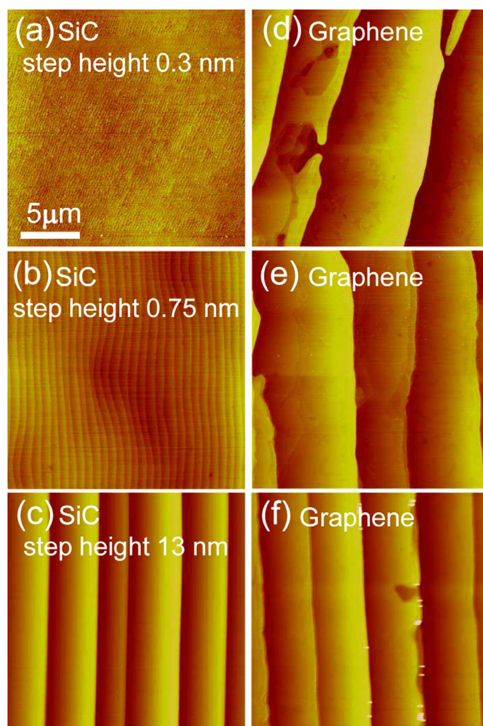

FIG. 1. (Color online) AFM images of (a) a non-etched SiC(0001) surface (0.3 nm step height), (b) a H-etched surface with step height of half $c_{6H\text{-}SiC}$ (0.75 nm), and (c) a H-etched surface with large steps (13 nm high), all obtained before graphene preparation. The respective AFM images obtained after graphene growth are shown in (d), (e) and (f).

the surface of a sample H-etched at 1400 °C. In this case, step heights equal to half $c_{6H\text{-}SiC}$ (0.75 nm) and 0.67 μm wide terraces are observed. A sample with larger step dimensions (1.5 nm step height and 1.2 μm terrace width) was also studied (not shown). The morphology of the SiC surfaces shown in Figs. 1(a) and 1(b) after EG formation is presented in Figs. 1(d) and 1(e), respectively. In both cases (as well as for the other sample whose results are not shown here), it is observed that after the EG preparation, the surface is composed of graphene macro-terraces with widths of about 5.5 μm and step heights of about 6 nm in average. Therefore, the results reveal that even for SiC surfaces with different initial

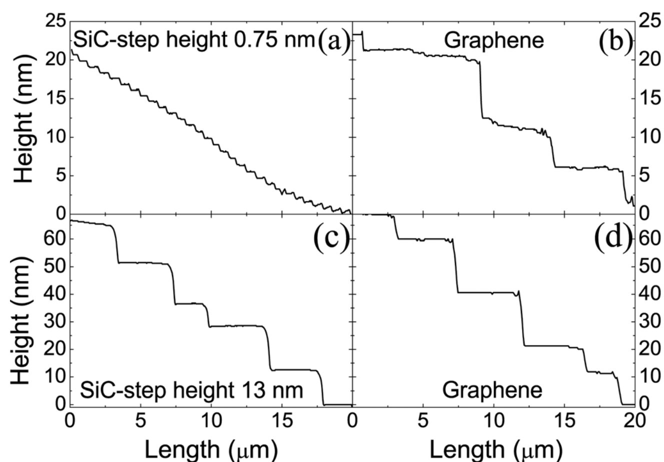

FIG. 2. Comparison between the profiles of the SiC stepped surface with initial step height of half $c_{6H\text{-}SiC}$ (0.75 nm) and terraces with 0.67 μm in width before (a) and after (b) graphene growth, and for the stepped surface with step height of 13 nm before (c) and after (d) graphene growth, where additional step bunching during graphene formation is not observed.

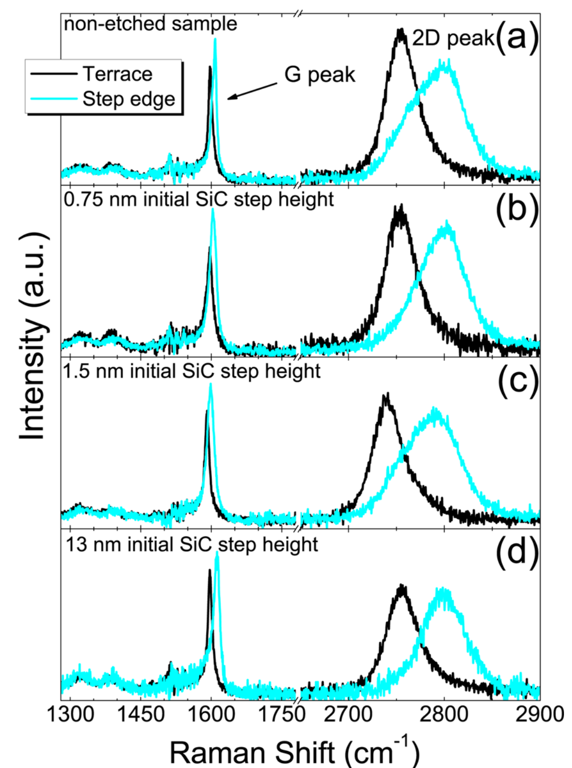

FIG. 3. (Color online) Raman spectra of the graphene samples prepared on different stepped SiC surfaces measured on the terrace and on the step edge.

step configurations, the final graphene surface that is formed as a result of an additional step bunching process exhibits a very similar morphology.

A different scenario is presented in Figs. 1(c) and 1(f). The AFM image of a SiC surface obtained after H-etching at 1550 °C (Fig. 1(c)) shows a stepped surface with average step height of 13 nm and terrace widths of 3.7 μm. The AFM image of the same sample after the EG formation (Fig. 1(f)) is quite similar to the initial etched surface. Interestingly, the average values of 13 nm for the step height and 3.7 μm for terrace width remain the same, meaning that further step bunching during graphene growth did not take place. The AFM profiles (see Fig. 2) for the surfaces of two different samples clearly show the additional step bunching (Figs. 2(a) and 2(b)) and its absence (Figs. 2(c) and 2(d)) during graphene preparation. This suppression may be due to the fact that the SiC surface containing steps of this height after etching has already reached a configuration of minimum surface free energy,[20,21] which for the other samples could only be achieved during the EG formation process. Even though no additional step bunching is observed, movement of steps along the surface during graphene growth cannot be excluded[17] and further investigations are necessary in order to clarify this aspect.

In order to analyze the effect of the different initial SiC surface configurations and the absence of the step bunching process on the graphene structural properties, Raman measurements were performed at the terrace and step edge regions for each sample after EG growth (Fig. 3). The spectra were recorded with a spatial resolution of 1 μm using the 413.1 nm-line of a Kr^{+} ion laser for excitation. For the spectra shown in Fig. 3 the Raman signal from the SiC substrate has been subtracted from the original spectra. For all samples

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very similar spectra are obtained, independently whether the measurements were taken on terrace or step edge regions. It is worth to notice the presence of two small structures below 1500 cm^{-1}, one at 1325 and another at 1375 cm^{-1}. The former is an artifact induced by the subtraction of the substrate spectrum, as is the noise observed around 1500 cm^{-1}. On the other hand, the second one could also be the D peak, as this feature should be observed at about 1380 cm^{-1} for the used excitation laser wavelength. The presence of this peak is related to defects and domain boundaries in graphene and graphite.[22] However, the spectra exhibit a D peak with a very low intensity, indicating that the analyzed samples have only a small density of defects. This experimental finding reveals that the structural quality of the graphene film is not (or only weakly) dependent on the degree of additional step bunching during growth.

The 2D peak obtained for measurements at the terraces for all samples can be well fitted by one Lorentzian with a full width at half maximum (FWHM) of about 35 cm^{-1}, meaning that at this surface region the growth of monolayer graphene is predominant.[23] At the step edge the peak is broader (FWHM of 64 cm^{-1}) and asymmetric, with a shoulder appearing for lower wave numbers. The origin of the low-frequency peak might be the additional Raman signal from the terrace region (as the laser spot of 1 μm diameter always covers to some extent the terrace region). However the existence of bi- or even tri-layer graphene at the step edges could also explain the observed shapes of the 2D peaks, as previously reported in the literature.[16–19] The need of more than two Lorentzian functions to fit this peak, being one due to the terrace contribution, confirms the existence of more than one monolayer graphene at the step edge.

For measurements performed on terraces, the G peak is located at about 1596 cm^{-1} for every sample, while for the step edge regions it occurs at about 1605 cm^{-1}. This blue shift of 9 cm^{-1} is accompanied by a peak broadening of 3 cm^{-1}. A similar behavior is observed for the 2D peak which shifts from 2752 cm^{-1}, measured on a terrace, to 2800 cm^{-1} on the step edge. The blue shift observed for the G and 2D peaks reveals that there is a difference in strain[24] and/or charge carrier density[25] between those two surface regions. However, the blue shift of the 2D line is also related to the number of graphene layers, which is larger on the step edges, as discussed above. Thus, the observed peaks shift of 9 cm^{-1} (G peak) and 48 cm^{-1} (2D peak) cannot be used to determine the difference in strain and charge carriers density between these two surface regions, as the 2D peak position depends on a third parameter. Even though it is expected a difference in strain and number of graphene layers between the terrace and the step edge, both graphene regions have a good and comparable structural quality. The most important observation is that the presence or absence of the step bunching process during graphene formation does not influence the material structural quality.

In summary, we have studied the formation of EG on stepped SiC surfaces with different surface morphologies obtained by varying the temperature during H-etching. We observe that the additional step bunching, which is usually observed during epitaxial graphene formation on SiC(0001), can be suppressed when the initial SiC surface is composed of large steps of about 13 nm in height. By Raman spectroscopy we demonstrate that the suppression of step bunching does not influence the graphene structural quality or the number of grown layers, and is thus not an essential process of the graphene formation dynamics. The present results open perspectives on the formation of single-layer graphene with a pre-defined surface morphology, or even on the production of graphene nanoribbons at the large SiC step facets,[26] which here are obtained directly from the H-etching process.

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