Effect of etch and growth parameters on the properties of epitaxial graphene grown on 6H-SiC

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Abstract

Multilayer epitaxial graphene has been grown on the Si-face of 6H-SiC on-axis commercial substrates under high vacuum (< 3×10^{-5} torr) and at high temperature (up to 1900 ^{0}C), utilizing the standard sublimation growth technique [1] and a modified SiC rapid thermal annealing system which allows for excellent control of heating and cooling ramp rates. A number of different growth parameters have been systematically varied in order to ascertain their effect on the formation of epitaxial graphene, and both the initial substrate etch step and the subsequent high temperature growth step were found to have a significant influence on the properties of the graphene that grew over the SiC substrates. After growth, graphene quality and uniformity across the surface were measured by Raman spectroscopy using a 514.5 nm laser with a 700 nm spot size, while the surface morphology was probed in detail using atomic force microscopy (AFM) and scanning tunneling microscopy (STM).

Prior to graphene growth, the SiC substrates were first subject to an etch step to remove the surface damage which occurs during the mechanical polishing of the wafers. This step is generally performed in pure hydrogen gas [2], however in this case an Ar/H_2 forming gas mixture at 5% H_2 concentration was used, with the etching done at a pressure of 1000 mbar. The use of forming gas to pre-etch the SiC substrates was investigated by varying the etch parameters and observing the effect this had both on SiC surface morphology and on subsequent graphene growth. The morphology of the SiC substrate in particular was found to be highly sensitive to the etching temperature: while a 1600^{0}C etch step produced uniform single atomic steps across the surface, a 1550 ^{0}C etch step led to broad non-uniform terraces, and etching at 1650 ^{0}C led to significant bunching of atomic steps across the SiC surface (Figure 1a-c). Etching at even higher temperatures was found to lead to step roughening, as well as to the appearance of etch pits across the SiC surface [3].

After optimization of the SiC etch step with respect to morphology, systematic studies on the effect of a variety of different growth parameters on the quality of the resultant graphene layers were performed. These demonstrated that the Raman D peak at approximately 1380 cm^{-1}, associated with defects in the epitaxial graphene, could be minimized either by performing growths at a higher temperature (Figure 2a) or else by growing graphene over longer time periods at a lower temperature (Figure 2b). Although both methods were effective at reducing the D peak, graphene growth at too high a temperature was found to have highly deleterious effects on the surface morphology, with the formation of a high density of etch pits resulting from growth at 1900 ^{0}C (Figure 3a). This was in marked contrast to results from lower temperature growth runs, where the uniform SiC step structure formed during the etch step was found to be unaffected by subsequent graphene growth (Figure 3b).

In all cases, the FWHM of the 2D Raman peak was measured at between 65-75 cm^{-1}, by which it can be estimated that 2-3 layers of epitaxial graphene has been consistently grown on top of the SiC substrates [4]. This was verified by Auger spectroscopy, and STM/LEED was used to confirm the presence of epitaxial graphene on the SiC surface after the growth step (Figure 3c). This growth was found to be self-limiting, with longer growth runs or higher temperatures having no further effect on the width of the 2D peak. Ultimately, an optimal combination of good surface morphology and uniform graphene growth with a small associated Raman D peak was found to be obtainable only through the use of long growth times at an intermediate (1775 ^{0}C) furnace temperature.

In-depth studies on the morphology of the surface using STM also revealed the presence of numerous white lines representing wrinkles or folds in the epitaxial graphene film after growth on the SiC surface (Figure 3d). These features are believed to be caused by the differing thermal expansions of graphene and SiC, with strain release of the graphene during sample cooling being mediated by the formation of wrinkles across the surface [5]. A detailed investigation of this effect as a function of the sample cooling rates after high-temperature graphene growth will be presented.

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References

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Figures

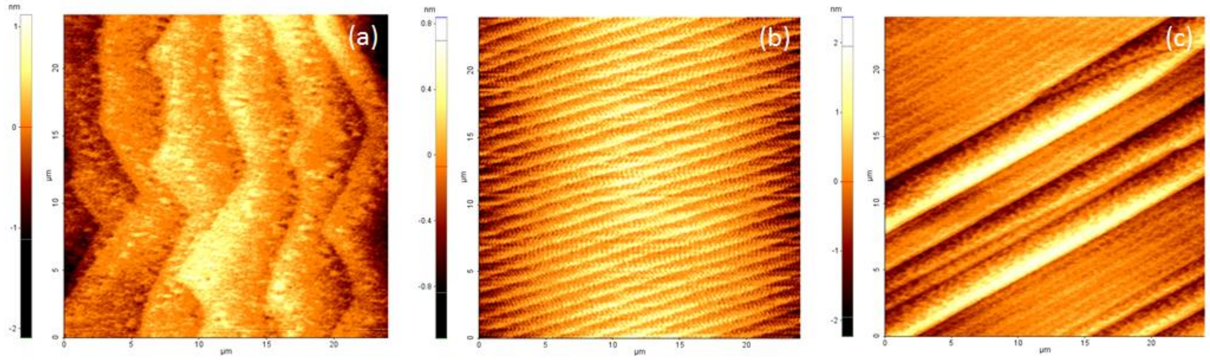

Fig. 1. 24×24 μm atomic force microscopy images showing the sensitivity of the SiC substrate to etching temperature. Samples were all etched in Ar forming gas with a 5% H_2 concentration, using the following etch parameters: (a) 1550 ^{0}C for 4 min; (b) 1600 ^{0}C for 4 min; (c) 1650 ^{0}C for 4 min.

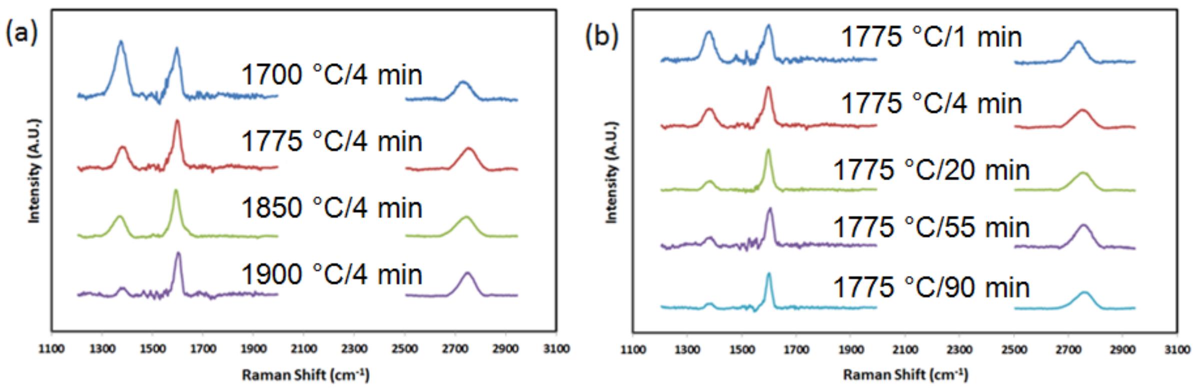

Fig. 2. (a) Raman spectra of epitaxial graphene on 6H-SiC as a function of the peak growth temperature; (b) Raman spectra of epitaxial graphene on 6H-SiC as a function of the growth time at peak temperature.

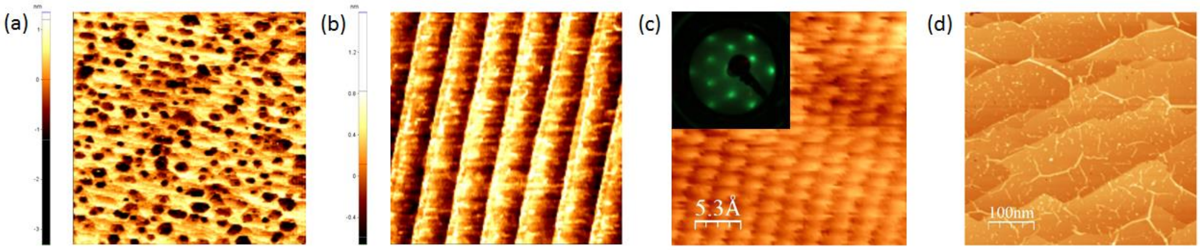

Fig. 3. (a) 10×10 μm atomic force microscopy image of the SiC surface after growth of graphene at 1900 ^{0}C for 4 minutes; (b) 10×10 μm atomic force microscopy image of the SiC surface after growth of graphene at 1775 ^{0}C for 55 minutes; (c) Atomic-resolution STM image of the epitaxial graphene layer after growth; (c, inset) LEED image confirming the presence of epitaxial graphene on the SiC surface; (d) STM image showing the wrinkling of the epitaxial graphene after growth on the SiC surface.