In-situ X-ray diffraction study of graphitic carbon formed during heating and cooling of amorphous C/Ni bilayers

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Published by the American Institute of Physics.
 Few-layer graphene has attracted intense interest as a possible material for post-silicon electronic devices due to its high mobility, two-dimensional structure, and tunable band gap.\textsuperscript{1,4} Methods for forming graphene such as mechanical exfoliation from graphite\textsuperscript{3} and decomposition of single-crystal SiC (Ref. 4) are not readily scalable to the wafer-scale dimensions that are expected to be required for semiconductor manufacturing. One potentially scalable method is metal-catalyzed chemical vapor deposition (CVD), in which graphene is formed on a metallic template layer exposed to a carbon-containing gas at elevated temperature (900–1000 °C). Several groups have shown that it is possible to grow few-layer graphene on Ni and transfer it to insulating substrate layers.\textsuperscript{2,5,6}

We have been investigating alternative metal-catalyzed graphene formation processes utilizing solid phase sources of carbon. In this approach, the carbon is not introduced from the gas phase but rather as one of the layers in an amorphous carbon (a-C)/Ni bilayer stack. It was hoped that this approach would provide films of quality comparable to those achieved by CVD but with better control over film thickness (since the carbon supply is fixed and finite). Our own results and those of Zheng et al.\textsuperscript{7} indicate that continuous films of few-layer graphene may be produced with this approach under certain optimized conditions.

The present work focuses on the kinetics and mechanism of multilayer graphene formation in a-C/Ni bilayer structures comprising a top layer of Ni over bottom layer of a-C disposed on a thermally oxidized Si substrate. Our initial expectation was that graphene would form by a simple dissolution/precipitation mechanism in which C from the a-C layer would dissolve into the Ni layer during heating and be expelled from solution upon cooling. We also find that graphitic C, once formed, can be reversibly dissolved by heating to T > 950 °C, and that non-graphitic C can be volatilized by annealing in H\textsubscript{2}-containing ambients. © 2010 American Institute of Physics. [doi:10.1063/1.3397985]

In situ x-ray diffraction study of graphitic carbon formed during heating and cooling of amorphous-C/Ni bilayers

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We examine graphitization of amorphous carbon (a-C) in a-C/Ni bilayer samples having the structure Si/SiO\textsubscript{2}/a-C(3–30 nm)/Ni(100 nm). In situ x-ray diffraction (XRD) measurements during heating in He at 3 °C/s to 1000 °C showed graphitic C formation beginning at temperatures T of 640–730 °C, suggesting graphitization by direct metal-induced crystallization, rather than by a dissolution/precipitation mechanism in which C is dissolved during heating and expelled from solution upon cooling. We also find that graphitic C, once formed, can be reversibly dissolved by heating to T > 950 °C, and that non-graphitic C can be volatilized by annealing in H\textsubscript{2}-containing ambients. © 2010 American Institute of Physics. [doi:10.1063/1.3397985]
indicated that the graphitic carbon formed was present as a top surface layer.

Figure 1 shows ex situ XRD data for a-C(30 nm)/Ni(100 nm) samples before and after graphite formation induced by 900 °C/1 min RTA annealing in N₂ or Ar/H₂. Before annealing [Fig. 1(a)], 111 and 200 Ni peaks are present and graphite peaks are absent. After annealing in either ambient [Figs. 1(b) and 1(c)], strong graphite peaks appear and the Ni peaks become stronger and sharper, consistent with the Ni grain growth seen by optical microscopy.

The intensities and line shapes of the 002 graphite peak vary with the initial a-C layer thickness. As shown in Fig. 2 for the cases of 1000 °C/10 s RTA annealing in N₂ or Ar/H₂, the peak intensities are strongest for the a-C(30 nm) samples, about a factor of 10 lower for the a-C(10 nm) samples, and almost below the detection limit for the a-C(3 nm) samples. Similar results were seen for 950 °C samples, and almost below the detection limit for the a-C samples, about a factor of 10 lower for the a-C samples.

Figure 3(a) shows a contour map of in situ XRD data for a-C(3 nm)/Ni(100 nm) sample heated in He at a ramp rate of 3 °C/s. The implied crystallite sizes (computed from \(\lambda/\cos(\theta_B)\Delta(2\theta_B)\)) with the Bragg angle \(\theta_B\) in radians

\[15^\circ\] are 13 nm and 32 nm, respectively, in good agreement with the initial a-C thicknesses of 10 and 30 nm.

Figure 3(b) compares the integrated graphite intensity data for this sample with that of two others having thicker (10 and 30 nm) initial a-C layers. The graphite peak in Fig. 3(a) appears at \(2\theta \sim 30.5^\circ\) during heating, lending support to a metal-induced crystallization model. Graphite formation appears to be abrupt, with “widths” of formation (defined as the difference between the minimum and maximum in the second derivative of graphite peak intensity) of about 20–30 °C. Thinner a-C layers were observed to have both an earlier mean temperature of graphite formation (defined as the temperature at which the first derivative of the graphite peak intensity is a maximum), with values of \(~640^\circ\) for 3 nm, \(680^\circ\) for 10 nm, and \(730^\circ\) for 30 nm, as well as an earlier onset of graphite formation. The latter result was counterintuitive in that we expected the onset temperature to be independent of a-C layer thickness. We speculate that these differences may be due to interface energy effects or to the influence of interfacial or incorporated C on the time evolution of the Ni grain structure. For example, very thin a-C layers may be inherently more unstable, or some rate-limiting diffusion process necessary for Ni grain growth may be faster at SiO₂/Ni interfaces which might form (at least in localized regions) at an earlier stage of heating with thinner (and more easily consumed) a-C layers. However, it should be noted that the 3 nm a-C samples showed more variability, with some showing no detectable graphite XRD intensity at all.

![Figure 1](https://example.com/figure1.png)

**FIG. 1.** (Color online) Ex situ XRD scans of Si/SiO₂/a-C(30 nm)/Ni(100 nm) samples before (a) and after RTA annealing at 900 °C for 1 min in (b) N₂ and (c) Ar/H₂. Note the log scale and arbitrary baseline offsets.

![Figure 2](https://example.com/figure2.png)

**FIG. 2.** (Color online) Ex situ XRD scans over the 002 graphite peak of Si/SiO₂/a-C/ Ni(100 nm) samples with different thicknesses of a-C, after RTA annealing at 1000 °C for 10 s in ambient of N₂ or Ar/H₂: 3 nm a-C in (a) N₂ or (b) Ar/H₂; 10 nm a-C in (c) N₂ or (d) Ar/H₂; and 30 nm a-C in (e) N₂ or (f) Ar/H₂. The intensity scale is linear.

![Figure 3](https://example.com/figure3.png)

**FIG. 3.** In situ XRD results. (a) The 002 graphite peak in a Si/SiO₂/a-C(3 nm)/Ni(100 nm) sample heated in He at a ramp rate of 3 °C/s. (b) Graphite peak intensity data (integrated over the 2θ range 29.5° to 31.5°) for the same sample (line) compared to corresponding data for samples with initial a-C thicknesses of 10 nm (dashed) and 30 nm (dashed-dotted). The contour lines in (a) have a linear intensity spacing.
Figure 4 shows contour maps of in situ XRD data for the same samples as a function of time during heating to and cooling from 1000 °C at 3 °C/s. All three samples show a decrease in graphite intensity during heating from ~950 to 1000 °C, and an increase in graphite intensity during cooling from 1000 to ~950 °C. This clearly indicates that graphite formation during heating can also undergo a reversible dissolution/precipitation as the sample is thermally cycled. This effect is most pronounced for the thinnest a-C sample, as one might expect; while the amount of reversibly dissolved C is limited by the solubility of C in Ni and thus the same for all three a-C thicknesses, this dissolved a-C is a much larger fraction of the total amount of carbon for the thinner a-C samples.

In both the 3 and 10 nm a-C samples of Fig. 4, the graphite peak intensities reached during cooling are stronger than those seen during heating. Various factors might account for this, including (i) continued precipitation of dissolved carbon and/or (ii) changes in sample morphology and/or detection geometry resulting in the same amount of graphitic carbon having a stronger XRD signal. All three samples show shifts in 2θ peak position during heating and cooling, reflecting a thermal expansion/contraction of the lattice d-spacings (proportional to (sin θ)/λ) that is in close agreement with literature values for the graphite out-of-plane thermal expansion coefficient (~25 ppm/°C).

Given the similarity of the ex situ XRD results for N$_2$ and Ar/H$_2$ RTA treatments at 950–1000 °C, we were surprised at the absence of graphite in the in situ XRD signals from the 10 and 30 nm a-C samples annealed in ambient of N$_2$/H$_2$. We suspect that non-graphitic carbon is lost through formation of volatile hydrocarbons produced by carbon-hydrogen reactions when ramp rates are slow (~3 °C/s), an explanation that is supported by additional ex situ XRD measurements. For 30 nm a-C samples, we found that 550 °C/H$_2$ furnace annealing in N$_2$/H$_2$ produced no graphite signal, whereas the same anneal in N$_2$ produced graphite intensities about a third of those found for RTA anneals of a fresh sample at 900–1000 °C. In addition, RTA treatments of 900 °C/1 min in N$_2$ produced no graphite in samples previously given the N$_2$/H$_2$ 550 °C/H$_2$ anneal. It was also found that 550 °C/H$_2$ anneals in N$_2$/H$_2$ performed subsequent to formation of graphitic carbon by 900 °C/1 min N$_2$ annealing had no effect on the graphite peak intensity, supporting the notion that the C removed by the H$_2$ is amorphous rather than graphitic.

In summary, we have used in situ XRD during annealing to examine the formation of graphitic carbon from a-C/Ni bilayers. It was found that a simple dissolution/precipitation mechanism cannot account for our observation that graphitic carbon is first formed during heating rather than cooling. While a dissolution/precipitation mechanism is present, it is seen only after graphitic carbon has already formed; the initial formation mechanism appears to be a metal-induced crystallization and layer exchange mechanism analogous to that seen with Al-induced crystallization of a-Si. It was also observed that low temperature annealing in H$_2$-containing ambient will volatilize non-graphitic carbon. This work was supported by DARPA under Contract No. FA8650-08-C-7838 through the CERA program. We thank C.-Y. Sung for management support, the Microelectronics Research Laboratory staff for their contributions to sample preparation, and J. Jordan Sweet for help with the synchrotron XRD experiments (supported under DOE Contract No. DE-AC02-98CH10886).