



Cross-sectional transmission electron microscopy of thin graphite films grown by chemical vapor deposition

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ABSTRACT

Graphene has been the subject of an extraordinary upsurge of interest due to its intriguing properties and potential applications. Recent work has shown that excellent electronic properties are exhibited by large-scale ultrathin graphite films, grown by chemical vapor deposition on a polycrystalline metal and transferred to a device-compatible surface. The properties of such multilayered graphene films could depend strongly on film thickness and uniformity. Unlike the other common methods for analysis in the literature, cross-sectional transmission electron microscopy (TEM) would provide direct, straightforward analysis of film thickness and quality, as well as provide a means to investigate specific defect structures (e.g. wrinkles). However, this approach has not often been pursued due to the sensitivity of graphite to the electron and ion beam damage in such a procedure. Here, an approach to creating cross-sectional TEM samples using a focused ion beam lift-out method is presented, along with the resulting TEM images of thin graphite films and several wrinkle defects. Samples removed from as-grown films on polycrystalline nickel and films removed from measured devices are presented. The benefits and limitations to this approach are discussed.

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1. Introduction

Graphene has recently been a subject of much interest as a potential platform for future nanodevices [1]. However, many of the approaches to creating quality graphene are neither readily scalable, nor industrially compatible. Chemical vapor deposition (CVD) and related surface segregation techniques are a potentially scalable approach to synthesize graphite films (even monolayer graphene) on a variety of metal substrates [2]. One of the most commonly used substrates is Ni (dating back to 1970s) [3]. The strong revival of interest in ultrathin graphite/graphene films grown by CVD on nickel largely arises from the demonstration that such films can be transferred to another substrate (by detaching and floating the film in an acid solution), creating many possibilities for electronic applications [4–9]. The structural properties of such films have been studied by a number of methods, including Raman scattering, X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), and transmission electron microscopy (TEM) [4–8,10]. An understanding of the structural quality and thickness of the graphite films is of paramount importance both in improving growth procedures and understanding the resulting films' electronic properties. Of the methods mentioned above,

only TEM of cross-sectioned graphite films would allow for direct measurement of the film thickness, quality, and uniformity. Unfortunately, it is especially difficult to fabricate cross sections of thin graphite films.

In this paper, cross-sectional TEM images of thin graphite films grown by CVD on poly-crystalline nickel will be presented. In addition to films prepared from as-grown graphite on nickel (Ni) substrates, films transferred onto amorphous silica (SiO₂) were examined. All cross section samples were fabricated using a focused ion beam (FIB) lift-out method. Among the advantages of this technique was the ability to remove the latter samples directly from a previously measured device, for direct comparison of device properties with the physical properties of the film. In addition, using a lift-out approach allows one to selectively remove a cross section from a region containing specific defects visible in the SEM, such as the wrinkles commonly seen in CVD-grown graphite [11,12].

There are very few examples of cross-sectional TEM imaging of graphite in the literature [13], presumably owing to the non-trivial sensitivity of graphite to ion and electron beam damage. Typical cross-section preparation techniques involve an ion milling stage, which can easily destroy the graphite. Furthermore, it has been shown that there is visible beam damage during TEM imaging with electrons above 120 keV in graphene-related materials, and that there are even changes in the electronic properties below 20 keV for prolonged exposure [14,15]. The result of both ion and electron beam effects will be demonstrated in this paper, and the resulting limitations in the

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analysis of cross-sectional TEM of graphite will be discussed. The techniques discussed here should be generally applicable to cross-sectional TEM imaging of graphite/graphene films fabricated on other substrates, such as epitaxially grown graphite on SiC [16].

2. Methods

All cross sections were fabricated on a FEI Nova dual beam FIB/SEM with gallium ion source, equipped with a Klöcke nanomanipulator. A protective layer of Pt/C was deposited locally in the FIB, including a primary layer of greater than 50 nm deposited with the electron beam, followed by a secondary layer deposited using the ion source [17]. Primary milling of the samples was performed with the ion beam operated at 30 keV, aligning the beam direction perpendicular to the sample surface. It is typical to perform final cleaning at a small tilt to the cross section surface, to compensate for the moderate wedged shape that results from milling at zero tilt. Additionally, a lower energy ion beam (e.g. 5 keV) is typically employed in an effort to reduce the thickness of the ion-damaged outer layer of the thinned sample. Both cases were examined, but for reasons that will be discussed below, the preferred results were obtained using a final cleaning stage at 30 keV and a zero incidence angle ion beam. To help compensate for the damage to the exposed surface of the graphene, samples were left intentionally thick (>100 nm). TEM images presented here were taken using an FEI Titan 80–300 operating at 300 keV, equipped with a Gatan Tridiem Imaging Filter. Zero loss filtering with a 10 eV window was used to improve contrast in some images.

3. Results and discussion

Several important conclusions can be drawn from images obtained in cross-sectional TEM, despite the effects of electron and ion beam damage (Fig. 1). The graphite film appears to have a thickness that is

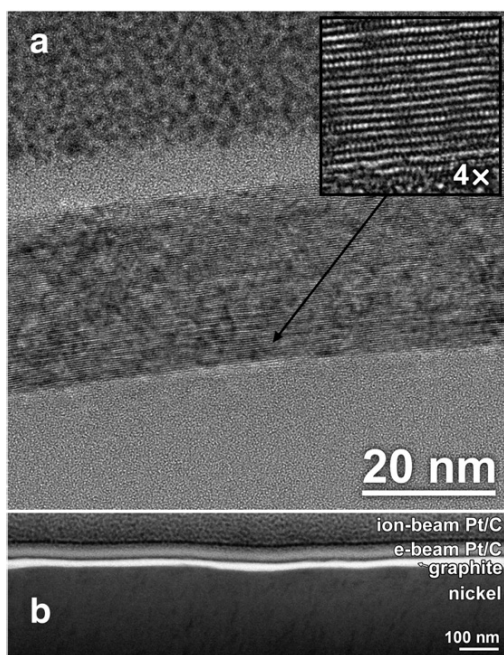


Fig. 1. (a) A thick region of the graphite film transferred onto amorphous silica as part of a device. The thin layer between the graphite film and the Pt/C protective layer is likely residual photoresist from the device processing. The magnified inset image has been processed using a rolling ball background subtraction filter to improve contrast [18]. (b) At lower magnifications, one can see that the graphite, as-grown on polycrystalline Ni, follows the surface of the substrate and not, e.g. the orientation of the underlying Ni (only one grain of the substrate shown in this image).

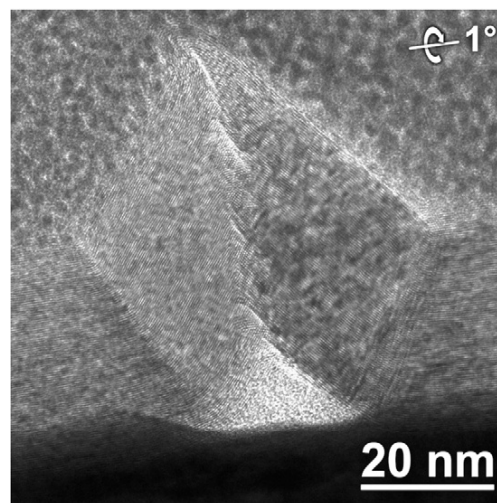


Fig. 2. A small wrinkle in graphite on Ni is shown at a 1° from the surface of the substrate. The tilt helps to emphasize the complexity of the juncture of the wrinkle, typical of other observed wrinkles of this size.

non-uniform at long-range, with regions observed from ~3–25 nm. Similar average thicknesses were observed in graphite on silica and the original Ni substrates. The graphite growth appears to have good quality locally, well oriented with the surface normal of the underlying support. In the as-grown graphite on Ni samples, it is clear that the graphite is oriented independently of the crystal structure of the nickel, in good agreement with past findings in the literature [19]. Lower magnification images clearly demonstrate that the graphite follows the contours of the surface of the polished Ni substrate (Fig. 1b). The orientation of the graphite even appears to be continuous across grain boundaries in the Ni.

One of the benefits of TEM analysis is the ability to investigate not only the quality of the film, but also the individual defects. The formation of wrinkles in graphite and graphene is well established in the literature, but the character of such defects has thus far only been studied by surface techniques, or in plan view TEM. Seen in cross section (Fig. 2), it becomes clear that interpretation of plan view images would be quite challenging. One can readily observe the sharp folds at the juncture of the wrinkle. This particular wrinkle, in as-grown graphite on Ni, has been intentionally imaged at a $\sim 1^\circ$ tilt from the surface of the Ni/graphite interface to emphasize the abrupt, uneven nature of the point of juncture. There appears to be some separation of the graphene layers in proximity to the defect, which is typical of the smaller wrinkles observed. The larger wrinkles observed in TEM also contain sharp junctures, but tend to fold more cleanly at a single plane (Figs. 3a and 4a). Additionally, although the number of data points is rather limited, observations suggest that the size of a wrinkle is somewhat correlated with the thickness of the graphite film on either side, with thicker areas of the film forming larger wrinkles.

One might wonder whether the wrinkle defects are merely artifacts induced by electron beam damage. Since the amount of electron beam damage increases with exposure time, a simple demonstration of its effects is to take a pair of images separated by an extended exposure time. A large, distinctly shaped wrinkle structure was chosen for clarity. The sharp wrinkle, as seen after minimal exposure, disappears almost entirely after ~ 2 min of exposure to the beam at normal imaging conditions (Fig. 3). In addition, the apparent ordering of the graphite is significantly diminished. The fact that these sharp defects are deteriorated by beam damage strongly implies that they are not initially created by said beam damage.

There were additional ripples apparent within the graphene layers, with height variations on the order of the interlayer spacing of the

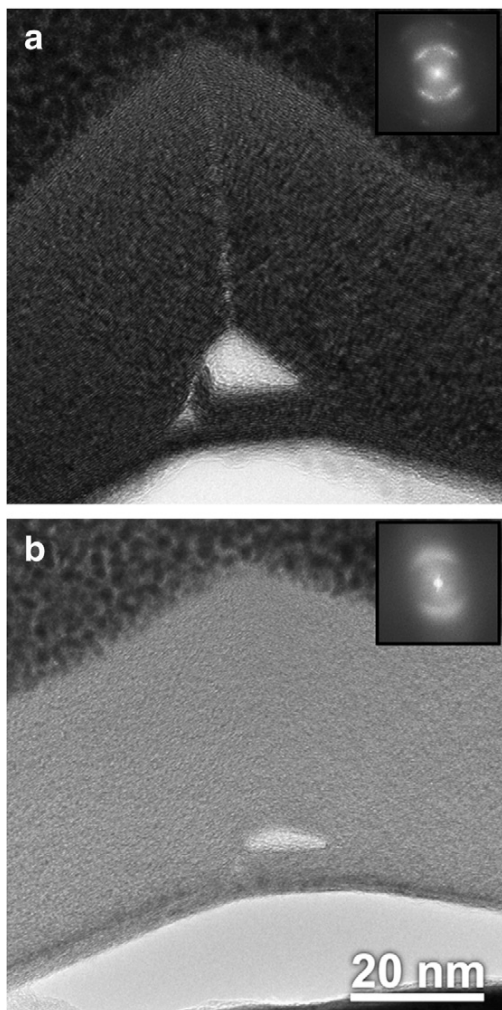


Fig. 3. A large, distinct wrinkle structure is shown before (a) and after (b) ≈ 2 min of beam exposure. Exposure was continuous, with the beam spread in a manner typical of normal imaging. The sharp line of folding at the juncture of the original wrinkle almost entirely disappears. This both demonstrates the difficulties of dealing with beam-sensitive graphite, and also strongly implies that such damage is not the source of the sharp wrinkles.

graphite. Results suggested that such defects could be the result of the electron beam. Small changes in these ripples were observed over consecutive exposure times of 0.1 s, suggesting that the irradiation leads to a constant breaking and reforming of the graphene layers. This does not prove that such ripples are not inherent in the graphite prior to exposure, as has been suggested in the case of single layer graphene [20,21]. At any rate, it seems safe to assume that images with limited exposure times are still broadly representative of the original structure of the graphite film.

More difficult to explain are some of the effects of sample preparation; namely, the effects of ion beam damage at different voltages and milling angles. The simplest issue is that the graphene appears to be significantly more sensitive than the materials directly above and below it. A sample removed from a device built on a silicon substrate is used for comparison, as the underlying silicon crystal makes for a good metric for comparison. For final milling with 5 keV ions at 3° , to a thickness of ~ 150 nm, the silicon substrate below the graphite appeared excellently cleaned and minimally damaged (as expected). The graphite, by contrast, showed more damage to layers near the top surface than those along the bottom surface (Fig. 4a). With further

cleaning at 5 keV, the apparent damage increased; once again, more so at the top surface (Fig. 4b). The underlying silicon, by contrast, simply appeared thinner and, if anything, cleaner. Another wrinkle was chosen to emphasize the changes in the graphite, and for ease of feature identification, but similar results are seen across the sample.

For top down milling, there is no reason to expect that the top surface of the graphite should receive more damage than the underlying layers. The layer of Pt/C deposited with the electron beam should protect the top surface of the graphite from any direct ion beam exposure. The 5 keV cleaning on the FIB used in this work must be performed at a slight angle (e.g. $3\text{--}5^\circ$) to the surface of the cross section to effectively remove the material. While this approach potentially exposes a greater amount of the graphite film, the geometry would suggest increased damage towards the bottom of the film, not the top.

Samples prepared from as-grown graphite on Ni samples were milled entirely at 30 keV at zero incidence angle (e.g. Fig. 3a). The extra damage at the top surface of the graphene is not observed. The overall thicknesses of the samples in Figs. 3 and 4a appeared comparable. Unfortunately, 30 keV cleaning at even 2° destroyed the entire film in a sample that was ~ 200 -nm thick before tilting. Further milling

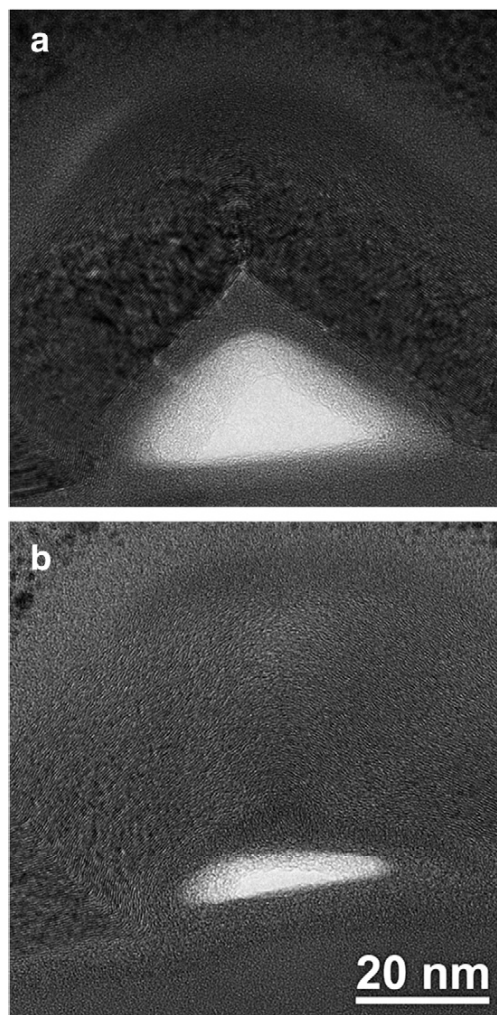


Fig. 4. Graphite appears to be especially sensitive to ion beam damage. Samples left intentionally thick (a) are quite sufficient for imaging, but further milling to less than 100 nm (b), even at low ion beam energy (5 keV) creates very significant damage to the graphite. Furthermore, milling at a slight angle, as is typical for lower energy milling, results in a gradient of damage from the top, to the bottom surfaces graphite, with more damage at the top.

the sample in Fig. 3 with 5 keV at 0° had no negative effects on the quality of the graphite layer. Unfortunately, as suggested above, it is not clear that it had any effect at all, somewhat limiting the value of this comparison. The simplest explanation would be that the thickness of the damaged region in the graphite is unexpectedly thick but uniform, and that cleaning at a slight angle led to a more wedge-shaped graphite cross section than expected. This would suggest that in those cases, the change in thickness from the bottom to the top of graphite film was comparable to the thickness of the damaged region.

A final consideration is the importance of the thickness of the protective capping layer. Given the above observations, it is perhaps unsurprising that the graphite layers were prone to separate when thinned. It was quickly realized that samples with thicker capping layers (greater than ~300 nm) demonstrated this unfortunate separation before the sample was winnowed to a usable thickness. One could imagine that the graphene film is under some initial in-plane strain (originating from differences in the thermal expansion coefficients between graphite and Ni, and correlated with the observation of wrinkles) which is partially relaxed during thinning. It is possible that a thicker capping layer is less compliant, resulting in enough unrelaxed strain for the graphene sheets to spall from one another.

4. Conclusions and future work

Graphene films are drawing a high level of interest for potential device applications, but an understanding of the thickness and quality of these films is of paramount importance. Much the most straightforward means of investigating thickness and defects in graphite films is direct imaging of cross sections using the TEM. The above results demonstrate that despite difficulties in sample preparation, it is possible to obtain TEM images with meaningful quality. These images help illuminate the structure of the wrinkle-like defects often observed in graphite films, as well as highlight the difficulty in analyzing such defects by alternative methods. These results also help confirm that there are unexpectedly good electronic properties even for modestly uneven films of tens of layers of graphene [7]. In particular, the ability to create cross sections using FIB lift-out methods allows for inspection of a film removed from within a device. The apparent sensitivity of graphite to ion beam damage can be somewhat mitigated by only milling with the ion beam parallel to the cross section, and leaving the sample greater than 150 nm thick. The specific effects of milling angle and ion beam energy require further investigation before the process can be improved. The electron beam damage caused by imaging in the TEM should be alleviated by working at lower voltages; but, as the preparation methods thus far result in fairly thick cross sections, lower voltages may not be suitable. Such an investigation will be pursued in future work. Work is also underway to study CVD graphene grown on Cu [22], which has recently been shown to enable the growth of large-scale graphene

with excellent uniformity [23], and on single crystalline Ni with different crystal orientations. We expect that cross-sectional TEM analysis can provide unique insights into understanding the CVD growth mechanisms of graphene.

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