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Focused ion beam milling: A method of site-specific sample extraction for microanalysis of Earth and planetary materials

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ABSTRACT

Argon ion milling is the conventional means by which mineral sections are thinned to electron transparency for transmission electron microscope (TEM) analysis, but this technique exhibits significant shortcomings. In particular, selective thinning and imaging of submicrometer inclusions during sample milling are highly problematic. We have achieved successful results using the focused ion beam (FIB) lift-out technique, which utilizes a 30 kV Ga^+ ion beam to extract electron transparent specimens with nanometer scale precision. Using this procedure, we have prepared a number of Earth materials representing a range of structures and compositions for TEM analysis. We believe that FIB milling will create major new opportunities in the field of Earth and planetary materials microanalysis, particularly with respect to ultraprecious mineral and rock samples.

INTRODUCTION

The introduction of ion milling in the 1950s for the preparation of mineral specimens for use with the TEM revolutionized the study of earth materials (Castaing and Labourie 1953; Paulus and Reverchon 1961; Barber 1970). Previous approaches to TEM examination of metals and biological tissues yielded unsatisfactory results when applied to the brittle oxides that comprise the bulk of the Earth and many meteorites. However, a new frontier opened in the microstructural analysis of Earth materials once it was shown that most minerals could be thinned to electron transparency with acceptably low levels of radiation damage by ion bombardment at ~6 keV. In conjunction with complementary techniques (such as dimpling and tripod polishing), Ar ion milling has evolved into the standard means of preparing TEM samples from minerals (Barber 1999).

Recently, Giannuzzi et al. (1999, and refs. therein) have shown that FIB milling may be used to prepare TEM specimens for metals, ceramics, composites, semiconductors, and biological materials. Here, we have extended the viability of this technique to a variety of mineral samples. FIB milling offers a host of capabilities beyond those exhibited by traditional Ar ion milling, including: (1) sample extraction from extremely small volumes of unpolished material; (2) site specificity at the submicrometer scale; (3) sample imaging by either secondary ions or electrons during the milling procedure; and (4) rapid processing of superhard materials. Our initial results indicate that FIB milling produces excellent TEM sections for a range of mineral structures and compositions, even friable clays. Therefore, FIB sample preparation heralds a dramatic advance in the microstructural analysis of mineral surfaces and particularly of ultraprecious materials, such as extraterrestrial specimens returned to Earth and historically significant gemstones.

ALTERNATIVES TO ION THINNING

Prior to the introduction of Ar ion milling, the major methods for preparing samples included electropolishing, ultramicrotomy, and crushed grain suspension. The last of these is the simplest and remains appropriate for certain applications. A rock or mineral sample is ground in an agate mortar in an ethanol solution, and a drop of the suspension then is deposited on a holey carbon film. Upon evaporation of the ethanol, the grid is ready for TEM inspection. The drawbacks to the technique are threefold: (1) all textural information is lost when the sample is crushed; (2) the typically small amount of thin edge limits the applicability of high-resolution TEM; and (3) some materials are less susceptible to cleavage than others. Diamond, for example, will grind an expensive corundum mortar rather than vice versa.

Ultramicrotomy involves the impregnation of a sample in a wax or resin block, which then is shaved into thin slices by a diamond knife. Although this technique is standard for biological TEM, it remains a specialized approach in the mineral sciences, suitable for soft clays, cosmic dusts, and bacterial-mineral interfaces (Eberhart and Triki 1972; Noguchi, 1998; Barker and Banfield, 1998; Paquette et al. 1999). The brittle quality of most ceramics leads to a "chattering" of the diamond knife as it sweeps across the specimen, which responds by fragmenting into a series of laminar sections. When the styles and concentrations of structural defects are an integral part of a

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mineral study, these artifacts are problematic. Electropolishing, to our knowledge, has never achieved a niche in the preparation of oxide ceramics for TEM. The acid brews required by this method work well for many metals (Thompson-Russell and Edington 1977), but they amorphize mineral surfaces too severely for subsequent crystallographic work.

Ar ion thinning

Argon ion milling eliminated many of the problems associated with the metallurgical and biological approaches to sample preparation, and with the availability of commercially produced ion mills in the 1960s, TEM characterization of mineral defects at the submicrometer scale markedly intensified, as is well documented in Wenk (1976). Nevertheless, Ar ion milling suffers from certain limitations. Most significant, the ability to select regions of interest is constrained to >1 mm^2 with conventional ion-thinning units. Even state-of-the-art preparation systems utilize beam diameters of hundreds of micrometers at typical operating voltages. Consequently, it is difficult to selectively thin individual features that are micrometer-sized and smaller.

In addition, specimens that undergo conventional Ar ion thinning typically require a prior stage of destructive sample preparation. In most cases, raw specimens are cut and polished as 30 μm petrographic thin sections from which 3 mm disks are extracted. Moreover, differential ion thinning of TEM samples can occur in heterogeneous rock specimens whose constituent minerals exhibit a range of hardnesses, such as clays embedded in feldspar. Uneven thinning can also be troublesome for monomineralic specimens with variable grain orientations, resulting in surface grooves that are easily mistaken for defect lamellae. Finally, conventional Ar ion milling may require extremely long processing times for materials that are superhard. Prethinning procedures, such as dimpling or tripod polishing (Bravman et al. 1988), may alleviate this difficulty, but application of these methods can prove technically challenging. For example, thin wafers (~30 μm) of diamond are not amenable to specialized mechanical thinning techniques unless one is willing to risk contamination with diamond polishing pastes. Standard diamond wafers may demand more than 100 h of conventional Ar ion milling before electron transparency is achieved.

Focused ion beam (FIB) preparation of TEM specimens

Focused ion beam milling of TEM sections has been exploited within the semiconductor industry over the last 10 years, primarily to ensure quality control by TEM examination of silicon wafers (Anderson et al. 1992; Stevie et al. 1995). The optics of the FIB instrument bear strong similarities to those of a scanning electron microscope. Rather than utilizing an electron source, FIB instruments typically employ a reservoir of liquid Ga, which is ionized and accelerated through 30 kV. Because the momentum of the Ga^+ ions is approximately 350 times that of electrons in an SEM, electrostatic rather than electromagnetic lenses are required to focus the ion beam. The resulting primary beam can be manipulated with nanometer precision at a target material to excavate the region surrounding a feature of interest.

Although this method has achieved outstanding results with semiconductors and other materials, its viability with respect to natural materials, including silicates, hydroxides, sulfides, and carbonates, has been unclear. Our first efforts with FIB milling to extract TEM sections from a carbonate-rich alteration veinlet within the Lafayette Martian meteorite were only partially successful (Vicenzi and Heaney 1999). Whereas the silicate host (olivine Fa_{67}) within the meteorite remained intact, Ca-rich siderite intergrowths were largely amorphized. These experiences suggested that some materials might not retain structural integrity when bombarded with high-energy Ga^+ ions.

In order to test the applicability of FIB milling to typical Earth materials, we prepared thin sections of a suite of minerals representing a range of structures and compositions. TEM sections of these samples and of some uncut materials were prepared with the "lift-out" technique refined by Giannuzzi et al. (1997, 1998). These specimens then were examined by conventional and high-resolution TEM, selected area electron diffraction (SAED), and energy dispersive X-ray spectroscopy (EDS).

Experimental methods

The specimens examined in this study included 8 standard petrographic thin sections of the following materials: (1) quartz [Hot Springs, AK; USNM no. R17684-2]; (2) plagioclase [An_{52}; Nain, Labrador]; (3) olivine [Fo_{90}; San Carlos, AZ]; (4) kaolinite [Sandersville, GA]; (5) calcite [UC Berkeley no. 135]; (6) pyrite [Bingham, UT; PSU EMS Y85.29]; (7) diamond (single crystal) [Orapa Mine, Botswana]; and (8) diamond (framesite) [Orapa Mine, Botswana]. An uncut specimen of the Murray carbonaceous chondrite [Murray, KY; USNM no. 1769] also was examined. Focused ion beam milling was performed with an FEI Model 200 TEM FIB system at the University of Central Florida.

The milling procedure adopted for this study is illustrated schematically in Figure 1, and an extraction sequence from a fracture surface of the Murray carbonaceous chondrite is presented in Figure 2. A linear Pt "strap" first is deposited on the surface of the specimen; this strap serves both as an indicator of the degree of flatness of the region as well as a protective coating for the foil during the milling process (Fig. 1a and Fig. 2a). Next, a 30 kV Ga^+ beam operating at ~20 nA excavates material from both sides of the Pt strap to a depth of 5 μm (Figs. 1b, 1c, and Fig. 2b). One of these trenches is sputtered with a broad entrant angle using a step-cut geometry to allow for the last stage of "undercutting," during which the film is separated from the matrix. Before undercutting and removal of the foil, the specimen is further thinned with a glancing angle beam at much lower beam currents of ~100 pA (Figs. 1d, 1e, and Fig. 2c). It is during this step that the foil is thinned to electron transparency, ideally ~100 Å in thickness. The sample then is rotated to plan view (Fig. 1f and Fig. 2d) for the undercutting procedure, which is achieved by ion beam perforation of the sample along the side and bottom edges (Fig. 2e). Figure 2f presents an edge-on view of a FIB milled specimen that is nearly ready for lift-out.

The removal of the foil from the host is performed ex situ at room pressure with the aid of a stereomicroscope and a hydrau-

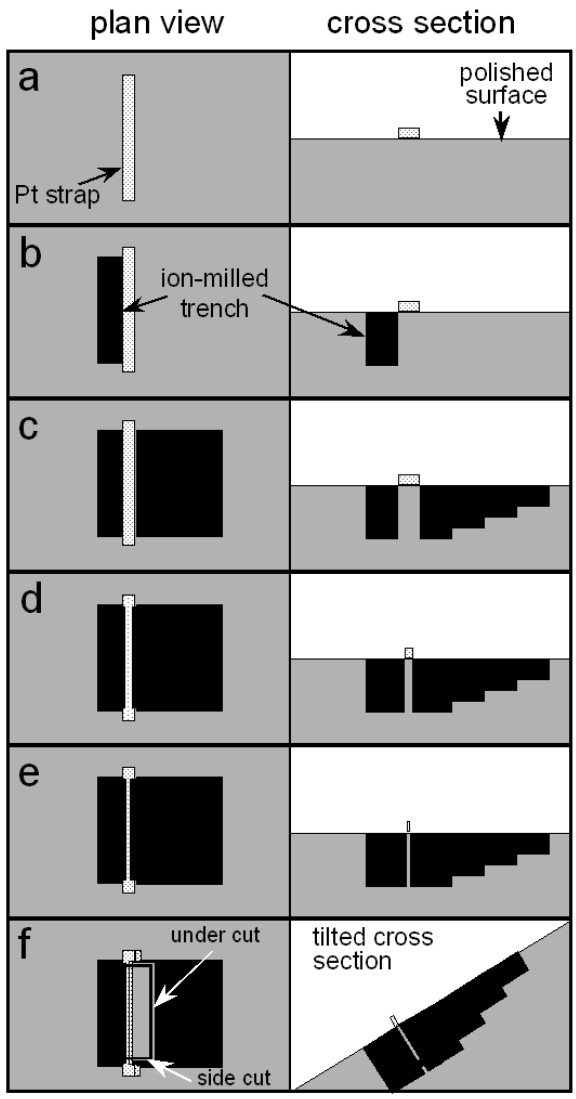

FIGURE 1. A schematic representation of the focused ion beam extraction sequence as detailed in the text, including (**a**) the deposition of a Pt strap; (**b** and **c**) the ion milling of trenches on both sides of the strap; (**d** and **e**) thinning of the specimen foil; and (**f**) tilting of the specimen for side and under cuts.

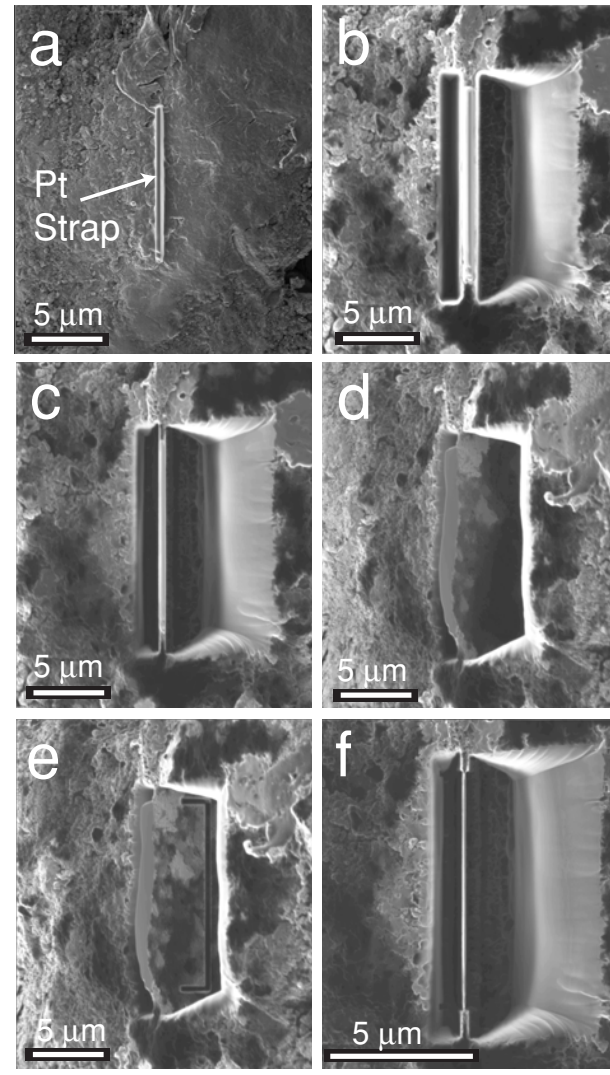

FIGURE 2. Ion-induced secondary electron images of the rough surface of the Murray carbonaceous chondrite at separate stages of extraction by focused ion beam milling. Images reveal the surface after the following preparation stages: (**a**) deposition of the Pt strap; (**b**) ion milling of the trenches; (**c**) thinning of the foil; (**d**) tilting of the specimen; (**e**) full undercutting and partial side cutting. A plan view of a fully thinned and partially cut foil is presented in (**f**).

lic micromanipulator. A drawn glass needle is directed to the excavation site, and the thin foil is extracted by electrostatic attraction to the needle. The samples, typically measuring ~20 µm × 5 µm × ~100 nm, then are deposited on to the membranes of 3 mm C-coated TEM grids. Transmission electron microscopy of our samples was performed with Philips 420 TEMs operating at 120 kV in the TEM facilities at the Johns Hopkins and Penn State Universities, and a Philips CM300 FEG TEM operating at 300 kV at the Johns Hopkins University.

RESULTS AND DISCUSSION

The high degree of site specificity associated with FIB milling is revealed in Figure 3, which depicts a section of the Lafayette meteorite following the extraction of several TEM foils. In addition to the exceptional precision offered by FIB milling, the sample volumes removed by this technique are extremely small. Consequently, FIB milling induces very little trauma to the specimen of interest. For these reasons, FIB milling is especially well suited to TEM foil preparation of materials that are unique, ultraprecious, and/or miniscule. Samples that meet these criteria would include interplanetary dust particles and returned samples from planetary missions, trace inclusions, and gemstones of such historical significance that more destructive methods are inappropriate.

In all cases, the samples prepared by the FIB lift-out technique in our study were well suited for TEM investigation. Foils

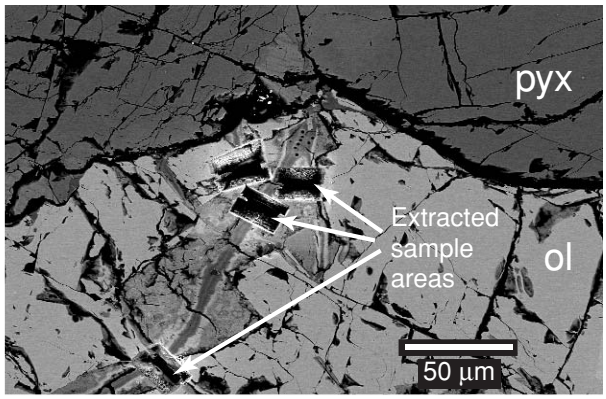

FIGURE 3. Backscattered electron image of an alteration veinlet in an olivine (ol) grain adjacent to pyroxene (pyx) in the Lafayette meteorite following the removal of several TEM foils by FIB milling.

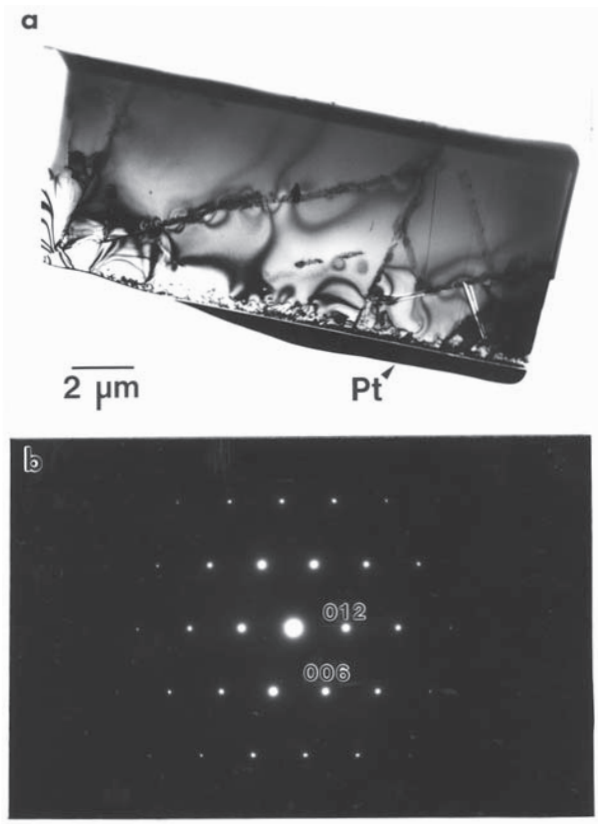

FIGURE 4. (**a**) A bright-field TEM image of an entire calcite section extracted by the FIB lift-out technique. (**b**) SAED pattern along [100] of the calcite foil.

were transparent to the electron beam, even at low operating voltages of 120 kV, and sample thicknesses were fairly uniform. For example, a 120 kV bright-field image of an entire calcite foil (Fig. 4a) reveals electron transparency over nearly the whole specimen, with a variety of defect microstructures intact. The corresponding SAED pattern (Fig. 4b) exhibits sharp spots, confirming the crystallinity of the foil. Similarly, crystal

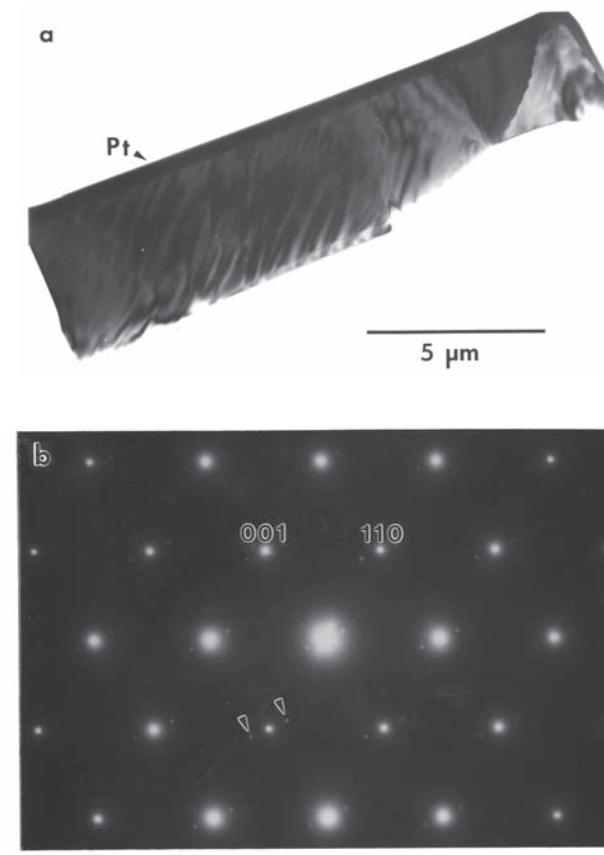

FIGURE 5. (**a**) A bright-field TEM image of a plagioclase section with Böggild exsolution features. (**b**) SAED pattern along [$\bar{1}$10] produced by plagioclase (An_{52}). Arrows point to superlattice "e" reflections.

packets within the FIB milled specimen of Georgia kaolinite yielded clear diffraction patterns, as did the other oxides, sulfides, and native elements that we examined. Bøggild intergrowths in labradorite are evident in bright-field images and SAED patterns (Fig. 5), which manifest distinct 34 Å superlattice spots oriented nearly but not exactly parallel to [22$\bar{1}$] (with $d_{22\bar{1}}$ = 3.44 Å). Consequently, even the subtle superlattice modulations characteristic of "e" plagioclase (Smith 1983) are preserved by FIB extraction.

Focused ion beam milling allows us to observe features that typically are lost during conventional ion thinning. Clays, for example, typically occur as a mélange of individual packets that can vary in thickness from tens of Ångstroms to micrometers within the same sample. TEM inspection of clays commonly involves procedures that disrupt the original bulk textures in order to maximize a preferred orientation such that all packets lie parallel to layering, followed by impregnation in resin. This approach is ideal for investigations that focus on smectite/illite diagenesis, but it can sacrifice textural information related to packing efficiency and void space at the microscale. By contrast, FIB extraction maintains textural integrity even of loosely consolidated clay mixtures, as revealed by the FIB milled foil of Georgia kaolinite (Fig. 6).

In addition, because the lift-out method is based on sample

excavation, FIB milling preserves surface features that normally are eliminated by Ar ion sputtering. The single crystals employed in this study were first prepared as standard polished thin sections, and FIB milled foils of these samples exhibited zones of extremely high defect concentrations, typically measuring ~200 nm in thickness (Figs. 4a and 7). These defective regions are artifacts of sample polishing, as is consistent with the observation of damage in ZnSe due to mechanical polishing for optical applications (Giannuzzi et al. 1998).

Finally, we note that FIB lift-out can yield TEM sections of even the hardest materials within 3 hours. An H_2O gas-injection system was used to enhance milling rates for polycrystalline and single-crystal diamond. Both sections were electron transparent, revealing sharp SAED patterns (Fig. 8a) and defect structures in bright-field images, such as nitrogen platelets and incipient cleavage (Fig. 8b). Indeed, the sections are sufficiently thin that high-resolution images were readily obtained with a beam energy of 300 keV (Fig. 8c). As conventional diamond preparation requires thin sectioning followed by very long milling times, the generation of diamond sections in hours represents a dramatic technical advance.

Focused ion beam milling of TEM sections poses some disadvantages. The instruments are quite expensive (more than 10 times that of a conventional Ar ion mill), and proper extraction technique requires practice: we believe that prior negative results involving FIB milling of minerals may be attributed to non-optimized milling procedures. In addition, total specimen areas are considerably smaller than those available in Ar ion thinned sections, though the speed of specimen preparation enables multiple extractions from a single sample. As revealed by EDS, Ga impregnation is unavoidable, and an amorphous surface coating of 25 to 50 nm envelopes each specimen. As seen in Figure 8, however, this coating does not hinder HRTEM

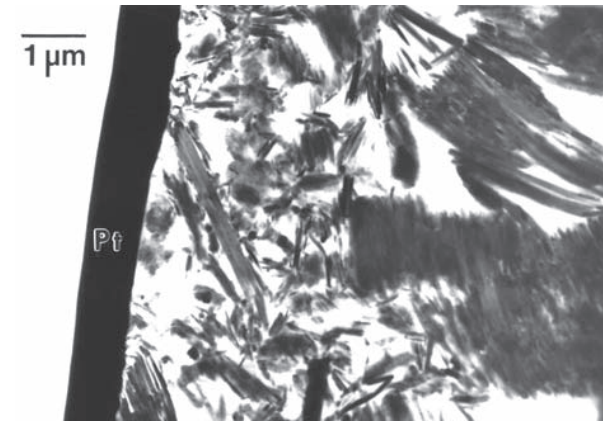

FIGURE 6. A bright-field TEM image of a FIB-milled kaolinite section with Pt strap.

FIGURE 7. A bright-field TEM image of a FIB-milled forsteritic olivine foil showing the defect-rich zone near the surface due to polishing.

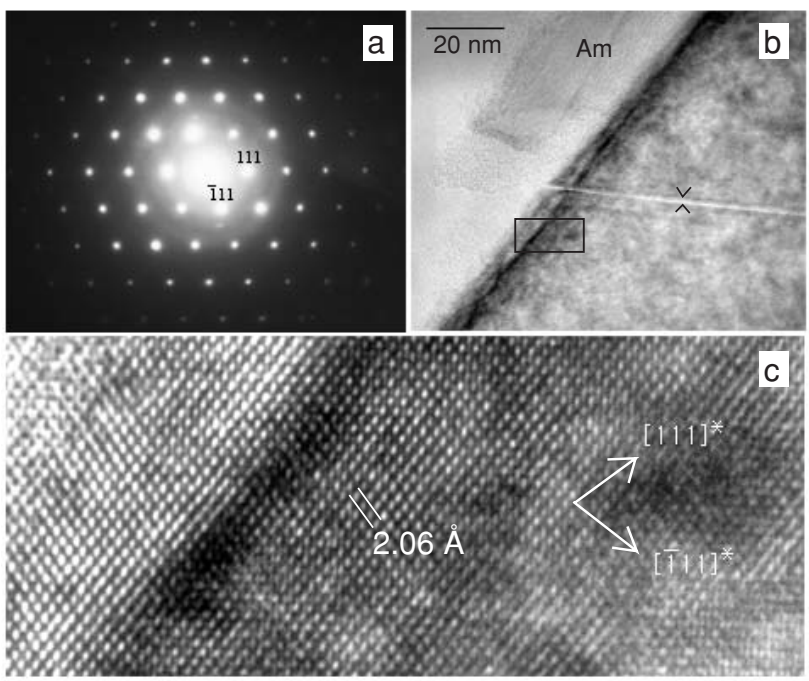

FIGURE 8. (**a**) Selected area electron diffraction pattern of FIB-milled, single-crystal diamond; (**b**) Bright-field TEM image of diamond, showing ~25 nm thick amorphization zone (Am) and incipient cleavage (arrowed); (**c**) High-resolution TEM image of boxed area in (B).

imaging. Finally, we estimate the low-end thickness of our samples as >500 Å, which is too great for electron energy loss spectroscopy. Nevertheless, we are confident that foil thicknesses will decrease as the technique is appropriately tailored to each mineral class. Because FIB milling allows the user to observe the extraction of sections from minute sample volumes without prior preparation, it will undoubtedly open exciting new avenues for TEM microanalysis.

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