

Combining Atom-Probe Tomography and Focused-Ion Beam Microscopy to Study Individual Presolar Meteoritic Nanodiamond Particles

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A method is presented for atom-by-atom analyses of individual nanometer-sized granular diamond particles (nanodiamonds, NDs) by atom-probe tomography (APT). A metal-deposition technique to affix the NDs is combined with the unique processing capabilities of a dual-beam focused-ion beam (FIB) microscope to obtain microtips suitable for APT. NDs extracted from the primitive carbonaceous Allende meteorite first identified by transmission electron microscopy (TEM) [1]. These NDs have been linked to a presolar origin based on isotopic anomalies of Xe and other trace elements, detected by bulk mass spectrometric methods [1,2] of large numbers of NDs, which, however, showed that the bulk ratio of $^{12}\text{C}/^{13}\text{C}$ is close to the solar system ratio, 89 [3,4]. In this correlative study of the same sample material, we apply APT to measure the isotopic carbon composition of individual Allende NDs [5].

Figure 1 illustrates the preparation technique. A 170 nm thick Pt(Al) bottom layer is deposited by ion-beam sputtering (South-Bay Technologies IBS/e) onto a polished Ni substrate disk, Fig. 1a. Next, the NDs are deposited by evaporating a droplet of de-ionized water with the NDs held in suspension by ultrasonic vibration of the Ni disk, resulting in a nearly circular deposition band, Fig. 1c, with individual NDs at the perimeter and larger clusters of NDs in the inner regions. The ND layer is then covered with a 170 nm Pt(Al) overlayer and a 400 nm Ni cover layer to provide a symmetric geometry for microtip preparation. The ND deposition band can be identified by SEM through the over- and cover layers, Fig. 1c. A cross-sectional cut, Fig. 1b, is made with a FEI Helios Nanolab FIB to locate the zone with individual NDs. A bar-shaped section is lifted-out in the FIB utilizing a standard technique [6], Fig. 1d, with an Omniprobe 200 micromanipulator, and transferred to a rotatable needle, Fig. 1e, for vertical reorientation. Sections of the rotated lift-out bar are mounted on standard silicon microposts [6], Fig. 1f. Employing annular milling patterns, a tip is formed centered on the deposition band within the region containing individual NDs in the microtip's apex, Figs. 1g,h. A Cameca LEAP4000XSi is used for APT analysis. Field-evaporation is assisted by focused ultraviolet (355 nm) laser pulses with an energy of 40–100 pJ per pulse, and a 500 kHz pulse repetition rate, at a base specimen temperature of 95 K.

Figure 2 is a 3D atom-by-atom APT reconstruction of about 25 individual NDs embedded in the Pt(Al) deposition layer. Figure 3 is the mass spectrum of the NDs, displaying the region of the peaks for ^{13}C and ^{12}C , singly and doubly charged ions. A ratio of $^{12}\text{C}/^{13}\text{C}$ of 63 ± 7 is obtained for C^+ , and 78 ± 10 for C^{++} . These values are close to the solar system ratio, 89, with differences attributed to the instrumental mass fractionation.

References

- [1] R.S. Lewis *et al.*, *Nature* **326** (1987), p. 160.
 [2] R.S. Lewis *et al.*, *Science* **190** (1975), p. 1251; S. Richter *et al.*, *Nature* **391** (1998), p. 261.
 [3] S.S. Russell *et al.*, *Science* **254** (1991), p. 1188; Marty *et al.*, *Science* **322** (2011), p. 1533.
 [4] Z.R. Dai *et al.*, *Nature* **418** (2002), p. 157.
 [5] F.J. Stadermann *et al.*, Lunar and Planetary Science Conference **XLII** (2011) #1595; P.R. Heck *et al.*, Lunar and Planetary Science Conference **XLII** (2011) #2070.
 [6] K. Thompson *et al.*, *Ultramicroscopy* **107** (2007) 131.
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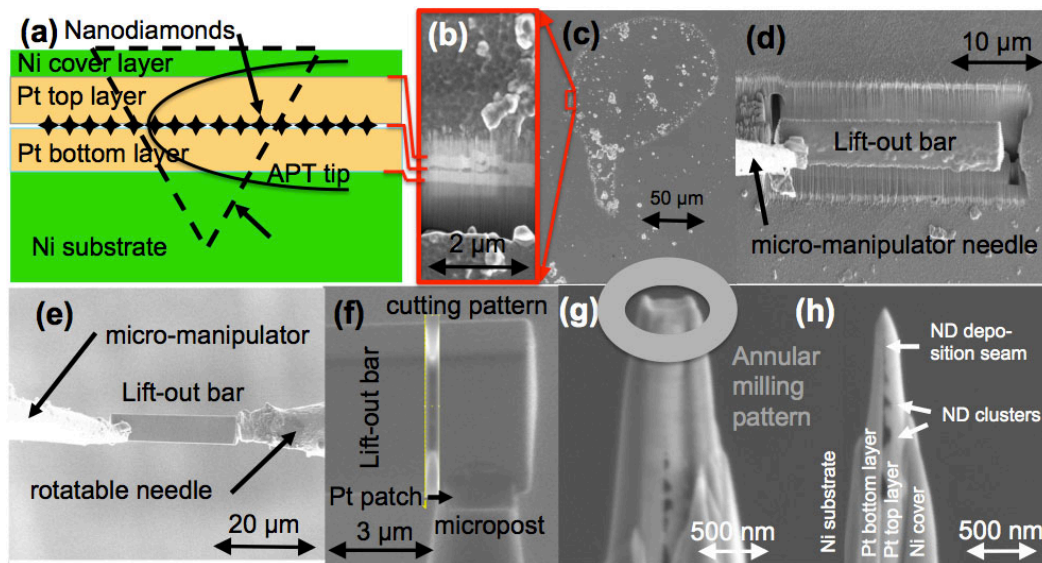


Figure 1. Schematic of deposition layering (a-c) to embed nanodiamonds in a Pt matrix. FIB lift-out (d); lift-out reorientation (e); tip mounting (f); tip sharpening (g); and the final microtip for APT (h).

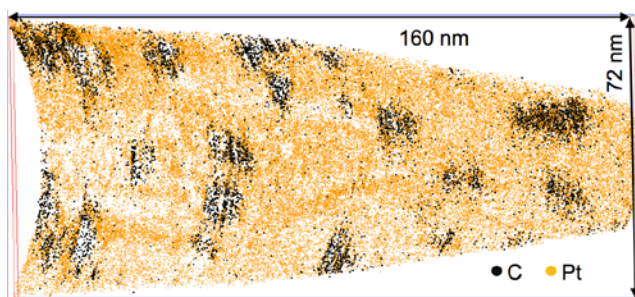


Figure 2. Atom-by-atom 3D reconstruction of individual nanodiamonds extracted from the Allende meteorite, for APT analysis embedded in a Pt(Al) matrix. C atoms are represented as black dots, and Pt atoms in orange. Only 5% of Pt atoms displayed for clarity.

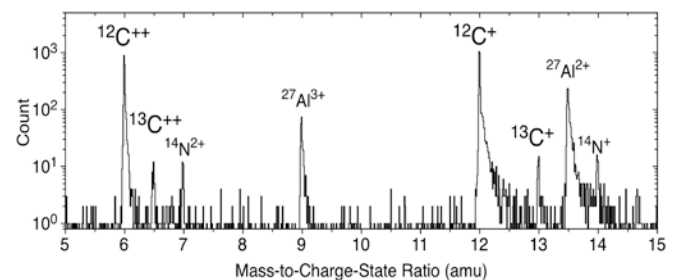


Figure 3. A partial mass spectrum with ¹²C and ¹³C isotopic peaks from nanodiamonds extracted from the Allende meteorite. A 5 at.% carbon iso-concentration surface was used to delineate the NDs in the reconstruction, Fig. 2. The Al peaks are from the Pt(Al) embedding material.