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MICROANALYTICAL CHARACTERIZATION AT HIGH SPATIAL RESOLUTION

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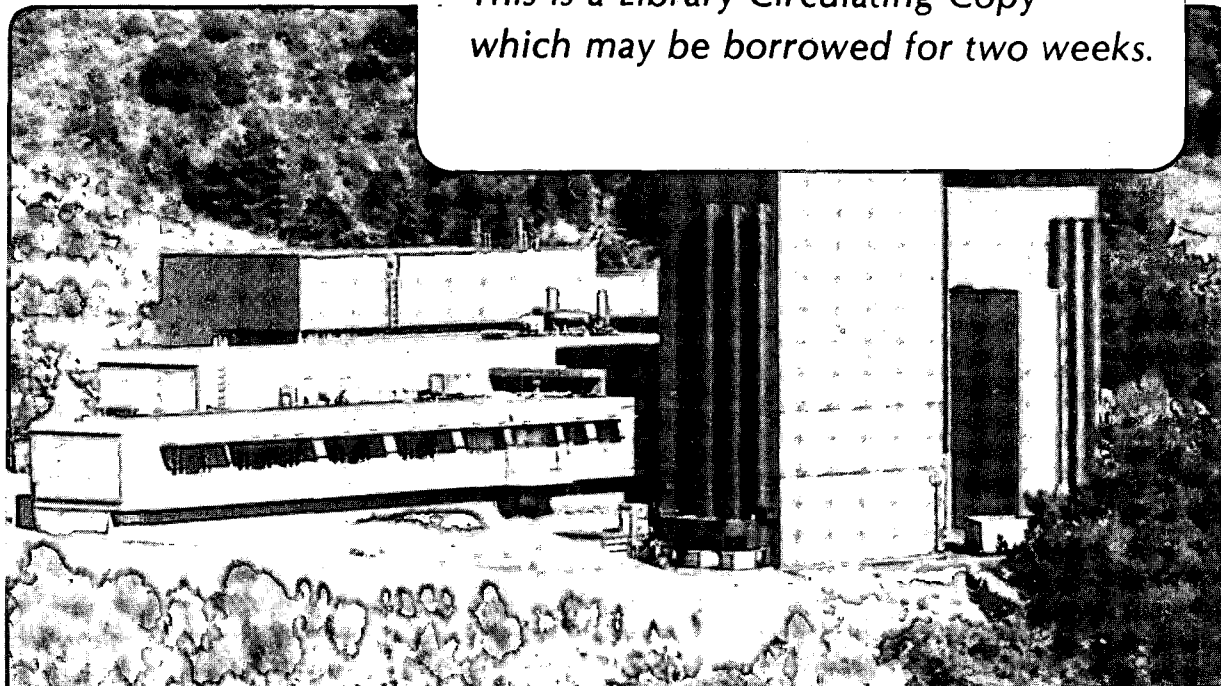
Structure and Bonding of Diamond and Diamond-like Materials: Microanalytical Characterization at High Spatial Resolution

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March 1988

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STRUCTURE AND BONDING OF DIAMOND AND DIAMOND-LIKE MATERIALS:
MICROANALYTICAL CHARACTERIZATION AT HIGH SPATIAL RESOLUTION

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Recent developments in the synthesis of single phase diamond films [1] and the observation of nanometer scale diamond-like particles in meteoritic residues [2,3] have generated much interest in the characterization of these materials. Of particular interest are the evaluation of parameters such as degree of crystallinity, defects, homogeneity, grain size, impurity content, bonding, electronic structure, etc. With the incorporation of fine probe-forming systems in an Analytical Electron Microscope (AEM) and the development of related diffraction, spectroscopic and imaging methods, it is possible to obtain precisely such structural and chemical information at high spatial resolution. Here we summarize the results of our studies of explosively compacted diamond particles, microwave plasma enhanced CVD diamond films and diamond-like residues of extraterrestrial carbon (C δ residue) by microdiffraction, energy dispersive x-ray spectroscopy and electron energy-loss spectroscopy, all using nanometer-scale electron probes and by electron spectroscopy for chemical analysis, a complementary bulk spectroscopic method. However, the characterization of the C δ residue is particularly emphasized.

All microanalytical spectroscopic/diffraction measurements were carried out on a JEOL 200CX AEM operating at 200kV, and fitted with a Gatan magnetic sector EEL spectrometer and a Kevex ultra-thin window lithium-drifted silicon EDXS detector. Electron probes ranging from 10nm in diameter were used.

High resolution electron micrographs were obtained using both the JEOL 200CX as well as the JEM 1000 Atomic Resolution Microscope capable of a point-to-point resolution of 1.7Å. To facilitate interpretation of the high resolution micrographs and to extract relevant structural information, some image processing was carried out [4]. The ESCA measurements were made on an SSX-100, using a high intensity Al rotating anode and a cylindrical electron analyzer. The Cδ residues used in our study were obtained by an acid and oxidant treatment [2] of fragments of the Allende CV3 meteorite. These residues were then suspended in alcohol and deposited onto holey carbon grids. All other diamond samples were prepared for electron microscopic observation using the same suspension process.

Preliminary characterization by SEM indicated the presence of 10-500nm size aggregates of diamond with very little porosity in the Cδ residue. A careful systematic microdiffraction experiment, using 20nm probes yielded both a Debye-Scherrer powder pattern and single crystal spot patterns of diamond (Fig. 1). The lattice parameter, based on these microdiffraction patterns, was determined to be 0.365nm; a 2% expansion of the lattice when compared to the ideal structure. High resolution lattice images (Fig. 2) of the {111} planes confirmed the presence of nanometer scale diamond particles.

Electron energy-loss spectroscopy (EELS) was found to be invaluable in the characterization of all these diamond materials. Both low loss plasmon excitations, corresponding to the collective excitation of the outer electrons, as well as the fine structure in the core loss edges were measured and interpreted. The low-loss spectra show that all the materials exhibit characteristic bulk diamond plasmon resonance peaks in the range of 30-34eV (Fig. 3). However, there are important observations to be made. The low pressure diamond film exhibits a distinct shoulder at 24eV. This feature was found to be thickness dependent, ruling out the possibility that it was due to a preferred interband transition. As the sample studied was approximately 20-25nm thick, for the particular transmission geometry, the excitation of a surface plasmon could be ruled out. These arguments lead us to conclude that this feature is a result of the hydrocarbon contamination on the surface of these films. For the Cδ residue, no shoulder was observed, suggesting that the sample surface was very clean. Moreover, some broadening of the plasmon half-width can be observed. However, the degree of broadening is consistent with the grain boundary damping associated with crystallite sizes of 5-10nm.

Figure 4 shows the C-k edges of low pressure diamond (LPD) and the C8 residue. The fine structure in the core edges (peaks at ~294 eV, ~307eV, ~320 eV)

correspond to the σ^* states of the sp^3 hybridized carbon in diamond. The experimentally observed spectrum is in good agreement with the calculated density of unoccupied bound states in diamond [5]. In the case of the C δ residue, one additional π^* feature normally associated with $1s \rightarrow \pi^*$ transition in graphite is observed at 286.8 eV. Similar π^* states have been observed in high resolution soft x-ray absorption spectra of the diamond (111) surface [6]. As described earlier, our analysis of the plasmon resonance data indicated no surface contamination. Therefore, the C $1s \rightarrow \pi^*$ transition observed can only be attributed to the presence of sp^2 carbon on the surface or interfaces of the nanometer scale C δ diamond particles. In fact, a good match was obtained between the experimentally observed spectrum and an artificial spectrum of 25% sp^2 and 75% sp^3 type carbon. This could be easily achieved if each 10nm diamond particle were to have about 6-8 monolayers of sp^2 carbon surrounding it. The accompanying relaxation to accommodate the elastic strains resulting from the topological reconstruction caused by the π bonding on the surface [7] of each particle would also be in agreement with the increase in lattice parameter, as measured by our microdiffraction experiment.

The results of the ESCA measurements are shown in Fig. 5. The C $1s$ high resolution data shown suggest that both sp^2 doubly bonded carbon and sp^3 tetrahedral (C-C) species were present in the C δ residue. The presence of $\pi \rightarrow \pi^*$ shake-up peak confirm the presence of sp^2 carbon and its line-width ($\sim 0.7\text{eV}$), corresponding to the instrument resolution, indicates no charging effects. Hence, computer generated gaussian peaks were fitted to the broad C $1s$ peak of the C δ residue. The carbon $1s$ peak, so deconvoluted, shows two principal components due to carbon atoms in the bulk (sp^3) and in the interfacial (sp^2) regions, in agreement with the EELS results.

We conclude from a careful analysis of our data from these complementary methods that the diamond residue is indeed diamond-like, but with a significant amorphous component arising from atoms at the grain-grain interfaces. It is hoped that similar high resolution microanalytical characterization studies would shed considerable light on many of the questions that arise in the synthesis of low pressure diamond films.

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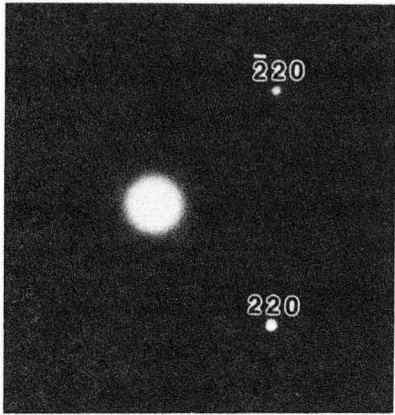
Fig. 1. Microdiffraction patterns obtained from nanometer scale diamond particles using 20nm electron probes. Single crystal patterns in three different zone axis orientations, i.e. (001, (011) and (112), are shown.

Fig. 2. High resolution image (a) of C δ crystallites showing crossed (111) fringes. A processed image to enhance the periodic features of the crystalline areas is shown in (b).

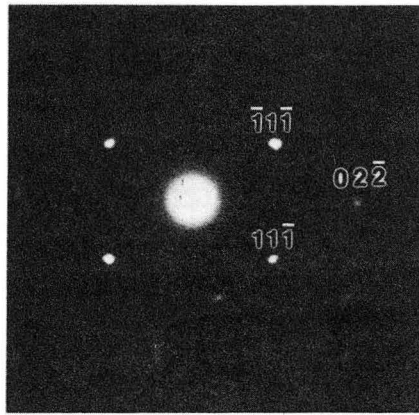
Fig. 3. Low loss spectra from (a) C δ diamond residue (sample: 15-30nm thick, 5-10nm grain size) and (b) synthetic low pressure CVD diamond (sample 20nm thick, 0.5-5mm grain size). In both cases characteristic diamond plasmon resonance peaks can be seen. However, considerable broadening of the plasmon half-width due to grain boundary damping in (a) and a feature corresponding to hydrocarbon contamination on the surface in (b) can be observed.

Fig. 4. Fine structure in the C-K edge of (a) C δ diamond residue and (b) synthetic low pressure CVD diamond. Both the raw spectra (continuous) and the deconvoluted single loss extractions (squares) are shown. The LPCVD diamond (a) is truly sp³ carbon and there is a good match between the observed spectrum and the calculated density of unoccupied states. The C δ diamond residue shows the presence of sp² carbon (C1s $\pi \rightarrow \pi^*$ transition) at the interfaces in addition to the dominant σ^* feature of sp³ hybridized diamond-like carbon.

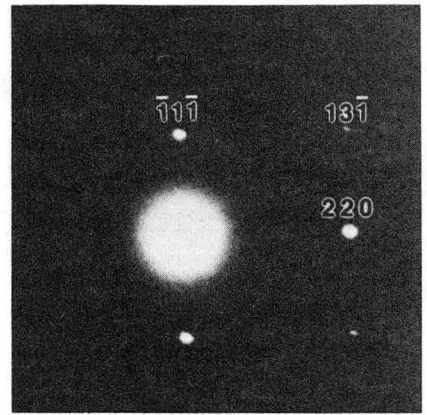
Fig. 5. ESCA spectra of the C 1s region of the two diamond materials. Dotted lines indicate computer generated gaussian peaks fitted to the observed data. (a) C δ diamond residue showing a satellite peak at 289eV. The broad C 1s peak can be deconvoluted into two: sp² and sp³ carbon. (b) the LPCVD diamond.



(001)



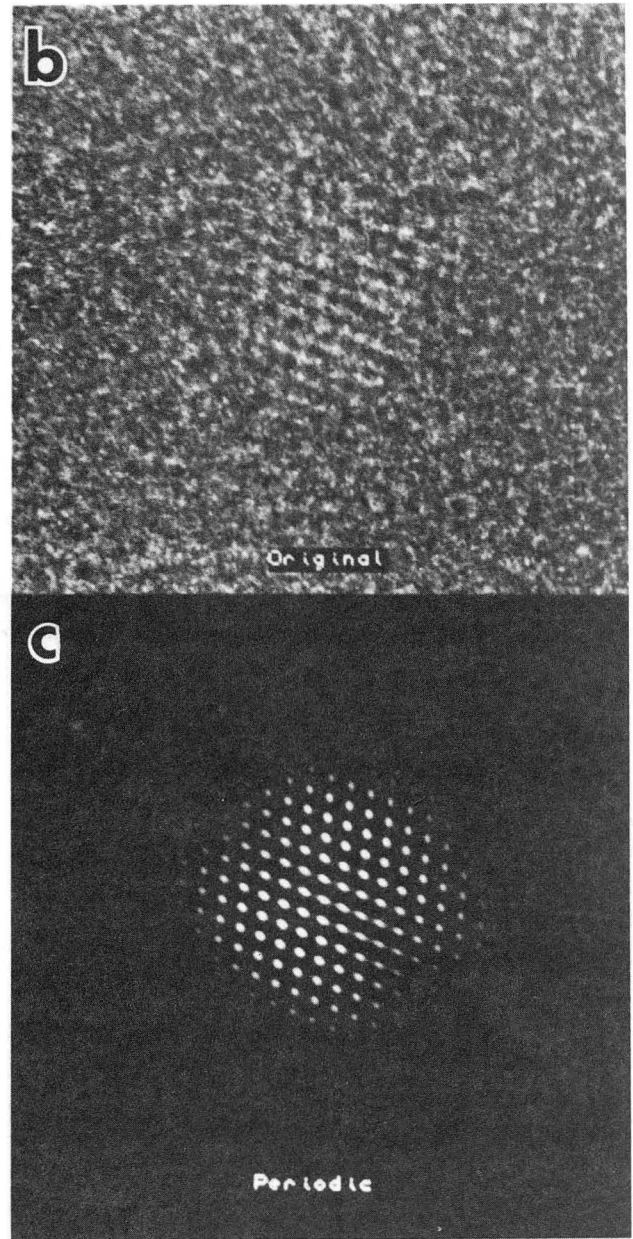
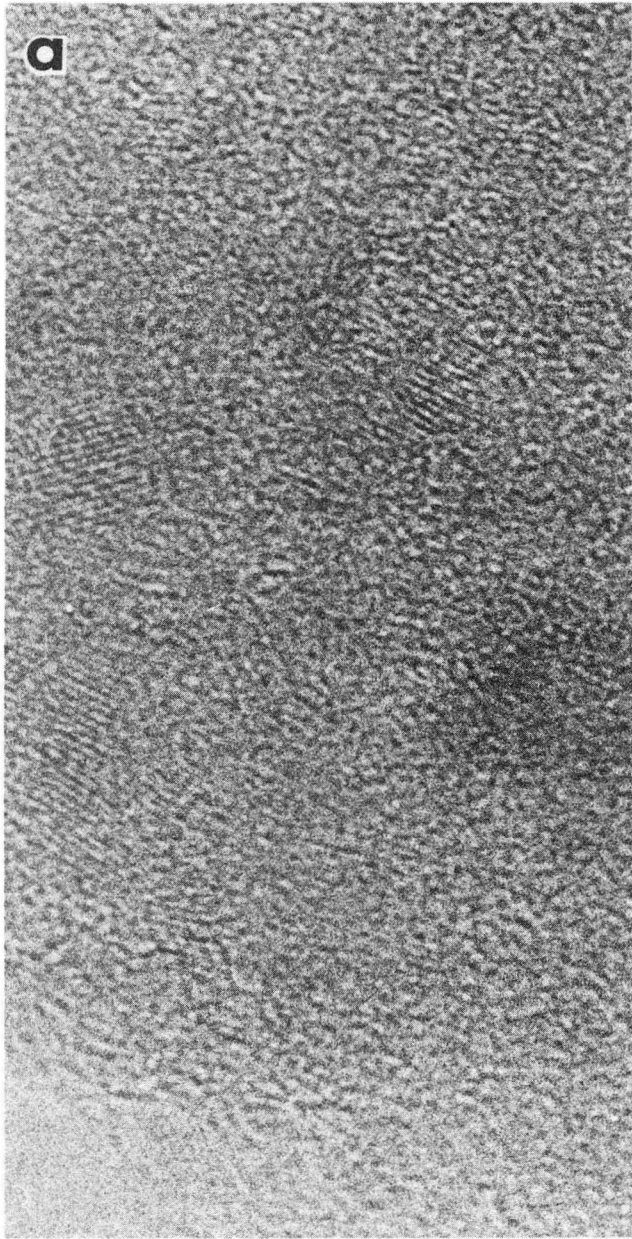
(011)



(\bar{1}12)

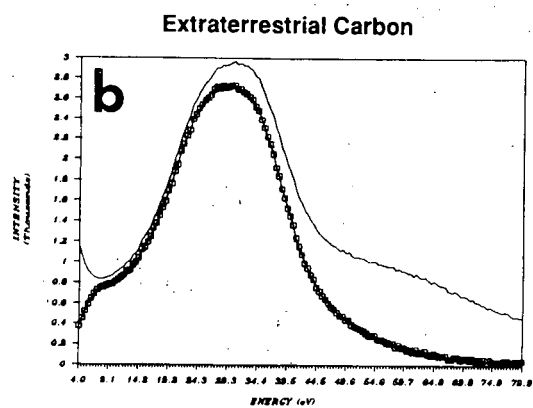
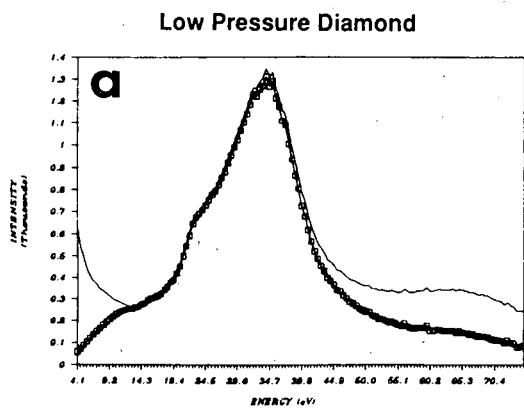
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Fig. 1



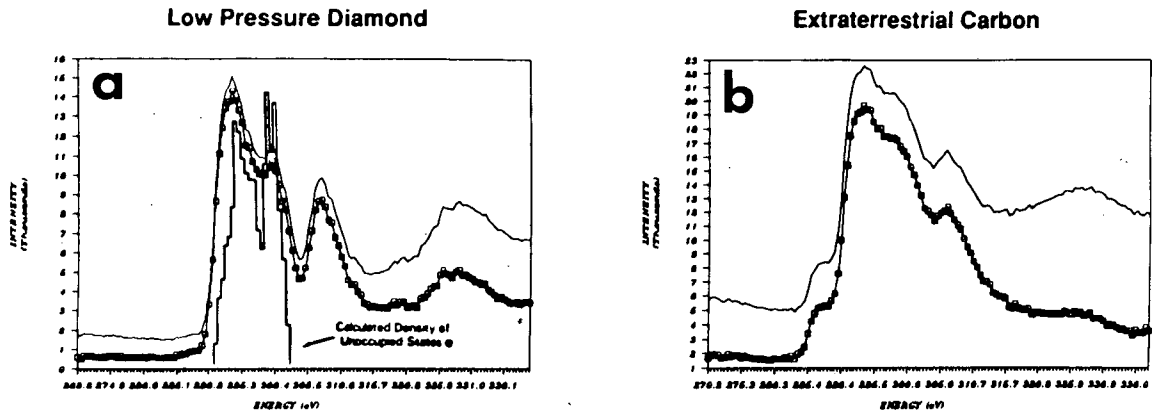
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Fig. 2



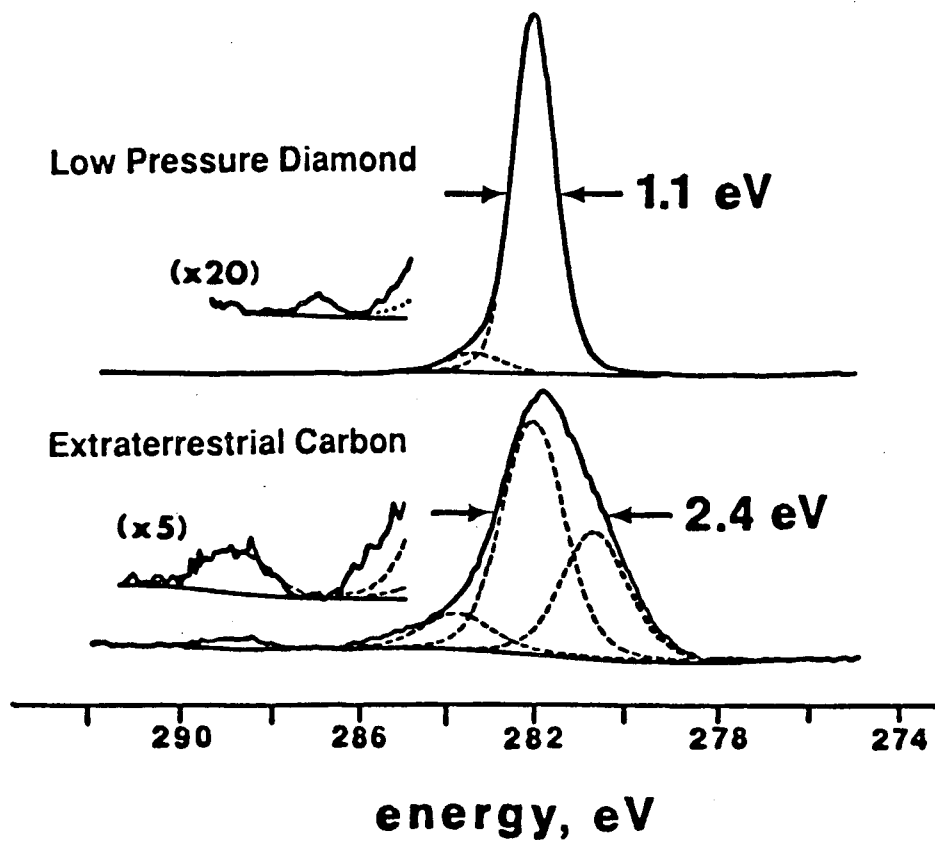
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Fig. 3



XBL 883-1002 A

Fig. 4



XBL 883-1004

Fig. 5

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