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R. Csencsits, D.M. Gruen, A.R. Krauss, C. Zuiker
Materials Science and Chemistry Divisions
Argonne National Laboratory
Argonne, IL 60439

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TEM STUDY OF DIAMOND FILMS GROWN FROM FULLERENE PRECURSORS

R. CSENCSITS[1], D.M. GRUEN[2], A.R. KRAUSS[2] AND C. ZUIKER[2]
[1]Materials Science Division, Argonne National Laboratory, Argonne, Illinois 60439
[2]Materials Science and Chemistry Divisions, Argonne National Laboratory, Argonne, Illinois 60439

ABSTRACT

Transmission Electron Microscope (TEM) techniques are applied to study the microstructure of diamond films grown from fullerene precursors. Electron diffraction and electron energy loss spectra (EELS) collected from the diamond films correspond to that of bulk diamond. Microdiffraction, high resolution images and EELS help determine that the first diamond grains that nucleate from fullerene precursors generally form on a thin amorphous carbon interlayer and seldom directly on the silicon substrate. Grain size measurements reveal nanocrystalline diamond grains. Cross section TEM images show that the nanocrystalline diamond grains are equiaxed and not columnar nor dendritic. The microstructure of small equiaxed grains throughout the film thickness is believed responsible for the very smooth surfaces of diamond films grown from fullerene precursors.

INTRODUCTION

Diamond films grown by plasma-assisted chemical vapor deposition using fullerene precursors [1,2] have been found to be extremely smooth with root mean square (rms) surface roughness of 20-40 nm using both laser reflectance interferometry (LRI) and atomic force microscopy (AFM) measurements [3]. The tribological properties of the films have also been investigated [4] and yield wear rates of 1.8×10^{-8} mm^3/N•m after 2.4×10^6 cycles using Si_3N_4 balls with 5N loadings were measured. These results indicate two orders of magnitude improvement over diamond films grown by conventional CH_4/H_2 methodologies, which typically have surface roughness in the micron range due to the micron size crystallites in the deposits. In a preliminary investigation using transmission electron microscopy (TEM) on these diamond films, an array of larger grains within a polycrystalline matrix of much smaller grains (< 20 nm) was reported [5].

The present investigation of microstructure using TEM was undertaken to better understand the nucleation and growth of diamond films grown from fullerenes as compared to films grown from methane.

EXPERIMENT

Diamond films were deposited in a microwave plasma chemical vapor deposition reactor (ASTeX PDS-17) as previously described [1,2]. The films were grown on single-crystal silicon wafers polished with 0.1 μm diamond particles to enhance nucleation density. Film growth was monitored in situ using laser reflectance interferometry to determine growth rate and stop growth at the desired thickness. The films were grown with 2 sccm H_2, 98 sccm Ar and C_{60} vapor (or methane), 100 Torr pressure, 1500 W of microwave power, and a substrate temperature of 850 °C.

The microstructure of the diamond films was studied using transmission electron microscopy (TEM). To observe and measure the diamond grain size distribution, plan-view TEM specimens were prepared; and to observe the grain size and shape along the direction of film growth, cross-section TEM specimens were prepared. Images and electron diffraction patterns were recorded in the Philips CM30 TEM operated at 300 kV and in the high-resolution JEOL 4000EXII TEM operated at 400 kV (point-to-point resolution is 0.17 nm). Electron energy loss spectroscopy (EELS) was performed using the Gatan parallel electron energy loss spectrometer (PEELS) on the Philips CM30 TEM.

A detailed description of our TEM specimen preparation can be found in reference [6]. Briefly our procedures are outlined here. Plan-view TEM specimens were prepared by gluing a 3 mm slotted copper grid to the diamond film side of the sample. The silicon substrate was mechanically thinned and then the center of the specimen was dimpled and polished to less than 10 μm. The specimen was ion milled from the silicon side until perforation with 6 kV nitrogen ions. In the areas observed in the TEM, only diamond film was present; all of the silicon substrate had been removed.

Cross-section TEM specimens were prepared by gluing sample pieces face-to-face with blank silicon pieces glued to the backs of the sample producing a four-layer sandwich. One side of the cross-section was polished and a slotted copper grid was glued to the polished side. The other side of the specimen was dimpled and polished to less than 10 μm. The specimen was finally ion milled from both sides until perforation with 6 kV nitrogen ions.

RESULTS

Figure 1 is a bright field plan-view TEM image showing the small equiaxed grains typical for the diamond films grown from fullerene precursors. Shown as an inset in Fig. 1 is the selected area electron diffraction (SAD) pattern formed from a 7 μm^2 area of the film. The continuous sharp rings indicate randomly oriented grains, and their spacings correspond to carbon in the diamond cubic form. In a bright-field TEM image, only those grains in favorable diffraction conditions appear dark with distinct boundaries. Grain size measurements from bright field images inherently count only those grains that are dark in the image, although this is not generally a problem so long as the grains are equiaxed.

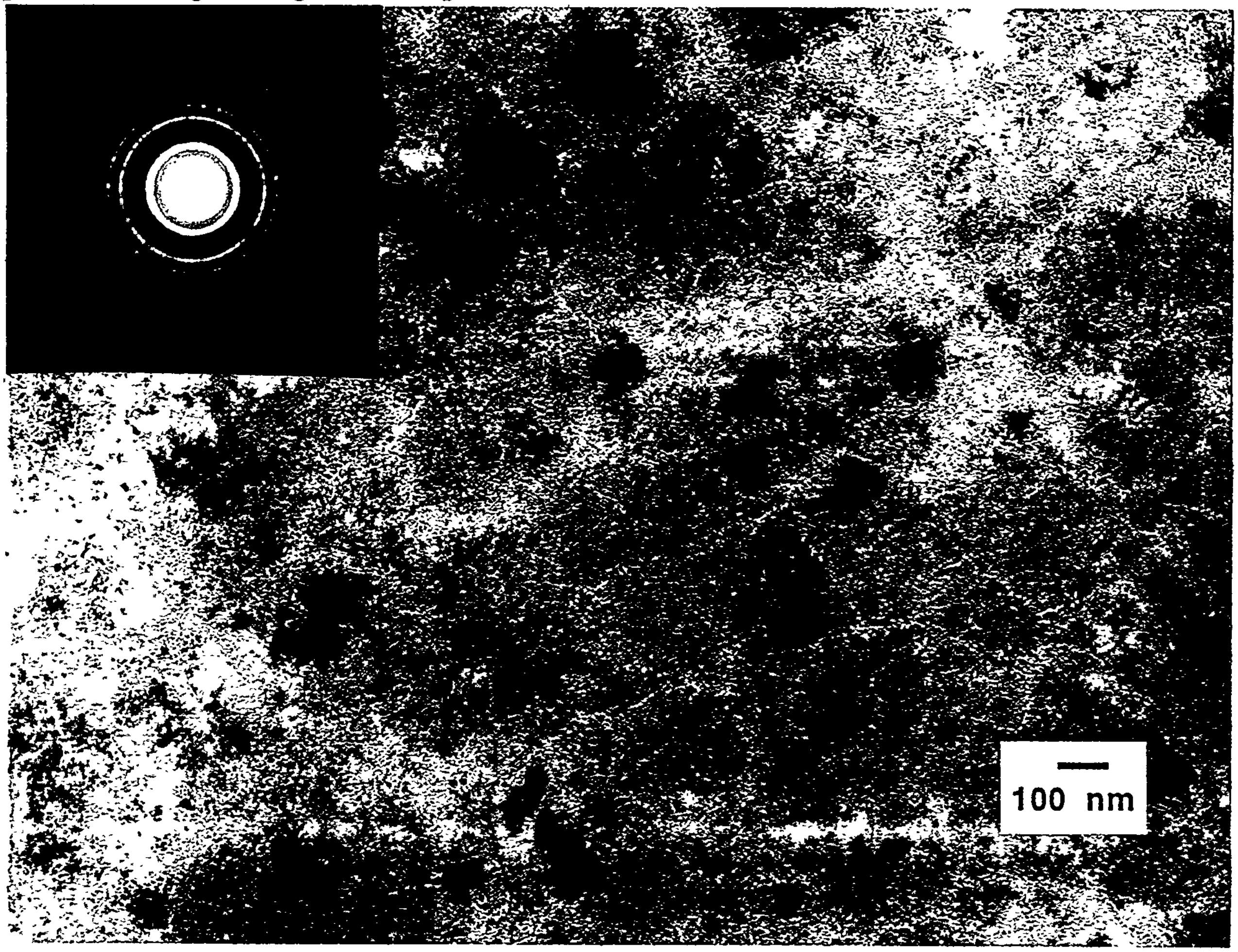

Fig. 1. Plan-view bright field TEM image showing the microstructure of diamond films grown from fullerene precursors. The electron diffraction pattern is inset and shows the random orientation distribution of the diamond grains.

Due to the small size of the grains and the dependence of grain visibility on diffraction condition in bright-field TEM images, the ASTM E112-85 standard grain size measurement procedures could not be used [7]. Instead, all discernible grains wholly or partially contained within a 0.53 μm^2 area on a TEM image were measured [6]. For the sample shown in Fig. 1, some 467 grains were measured. The minimum and maximum grain sizes are 3.2 nm and 103 nm, respectively. The median grain size is 12.7 nm, while the average grain size is 14.9 nm with a standard deviation of 12.9 nm.

The typical microstructure of the diamond films grown from methane in an argon plasma is shown in Fig. 2. Many dendritic grains are evident amongst the randomly oriented, equiaxed diamond grains. The random orientation of most grains is demonstrated by the SAD pattern; shown as an inset. For the equiaxed grains in the film the median grain size is 6.5 nm, while the average grain size is 7.7 nm with a standard deviation of 4.4 nm. This smaller grain size as compared to the film grown from fullerene precursors shown in Fig. 1 is also reflected in the more diffuse rings in the SAD pattern in Fig. 2 versus those shown in Fig. 1. The measurement of average grain size in the methane precursor film was done neglecting the dendritic grains. The dendritic grains are generally over 110 nm long and the fast growth direction is along the (111) planes. This dendritic microstructure of diamond films grown from methane in argon plasma is probably the cause of the greater rms surface roughness, typically 30-50 nm, of these films.

Fig. 2. Plan-view TEM image showing the microstructure and grain size distribution in diamond films grown from methane precursors in an argon plasma. The inset electron diffraction pattern indicates a random orientation distribution of the diamond grains.

A typical cross-section TEM image of a diamond film on a silicon substrate grown from fullerenes is shown in Fig. 3. Inset is the corresponding electron diffraction pattern consisting of the single-crystal silicon [110] pattern and three rings (111, 220, 311) of the polycrystalline diamond pattern. This diffraction pattern again indicates that the deposited diamond film consists of randomly oriented grains. In the image one observes that the diamond grains grown from fullerenes are generally equiaxed and not columnar nor dendritic. It is clear from this cross-section image that there is nucleation of grains throughout the thickness of the deposited diamond film.

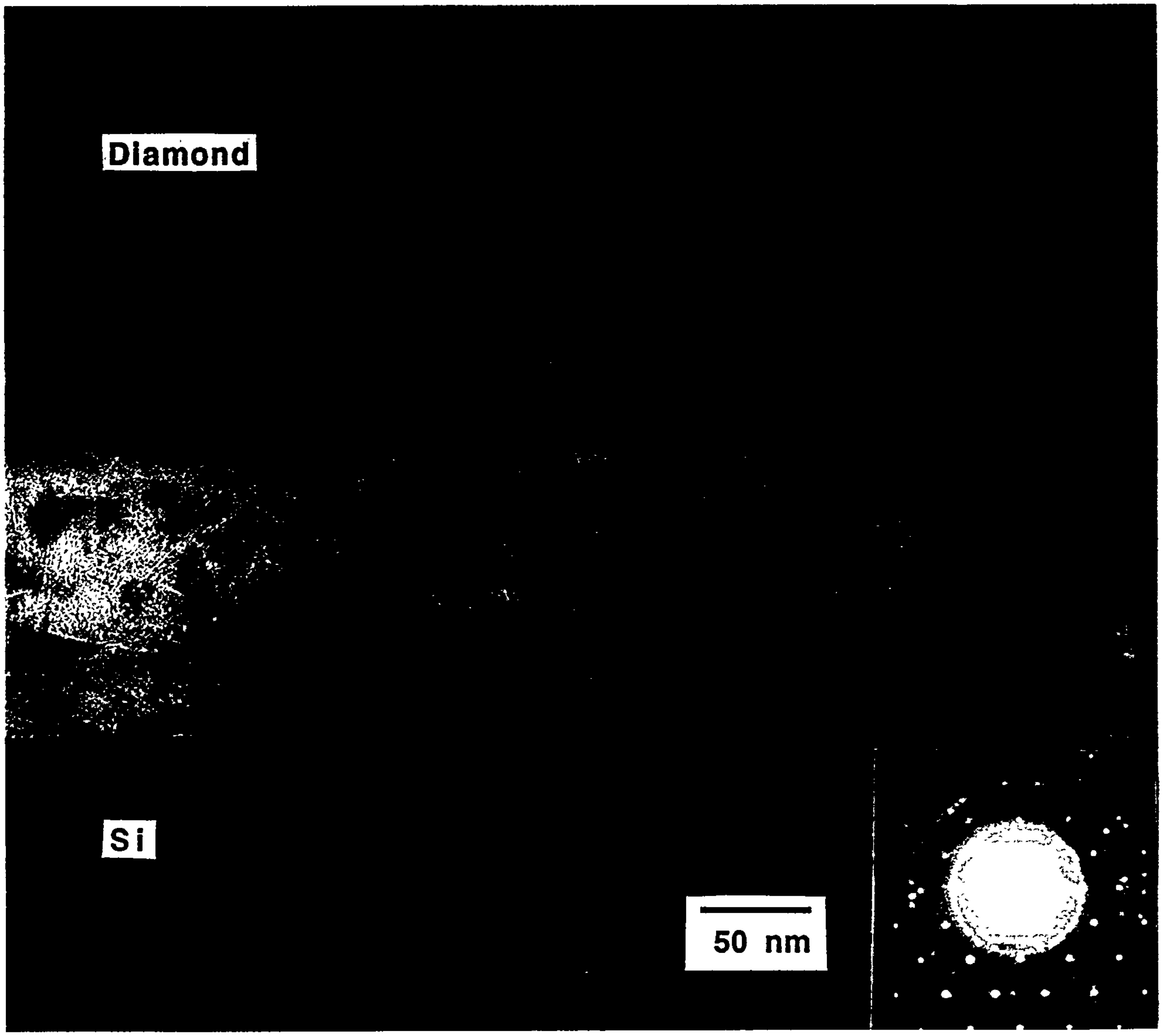

Fig. 3. Cross-section TEM image and SAD pattern of diamond film grown on silicon substrate.

To investigate the initial nucleation of the diamond film on the silicon substrate high resolution TEM images were taken from cross section specimens. Figure 4 is a cross section high resolution TEM image of the diamond/silicon interface on a film grown from C_{60} precursors. The silicon lattice fringes are separated from the diamond lattice fringes by a 16 nm thick layer of amorphous contrast. Microdiffraction verifies that this layer between the silicon substrate and the diamond film is amorphous. The natures of this amorphous layer and the diamond film were further probed using electron energy loss spectroscopy (EELS) in the TEM. The carbon k-edge EELS spectra collected from the diamond film and the amorphous interlayer are shown in Fig. 5. The EELS spectrum from the diamond film corresponds to that of bulk diamond. While the EELS spectrum collected from the 16 nm thick amorphous layer corresponds to amorphous carbon. An amorphous carbon interlayer has been identified in this manner in 3 of 4 samples studied. In the fourth sample the interlayer was one to two monolayers thick and discontinuous; in some areas the diamond appeared to nucleate on the silicon. In some cases nucleation of diamond occurred on diamond residue left from the scratching pretreatment, but most often it was on amorphous carbon.

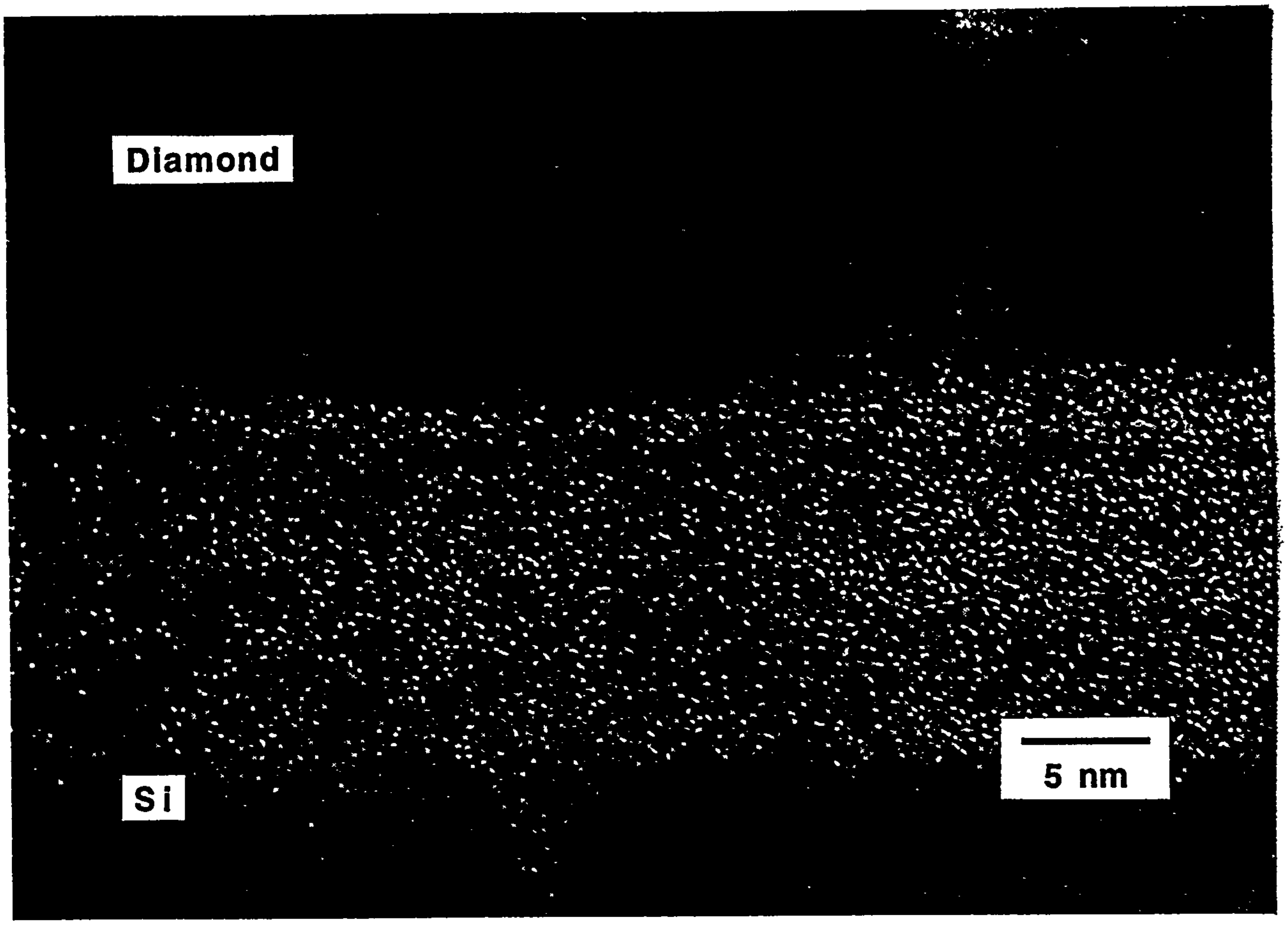

Fig. 4. A cross section, high resolution TEM image of the diamond/silicon interface showing a 16 nm thick amorphous interlayer.

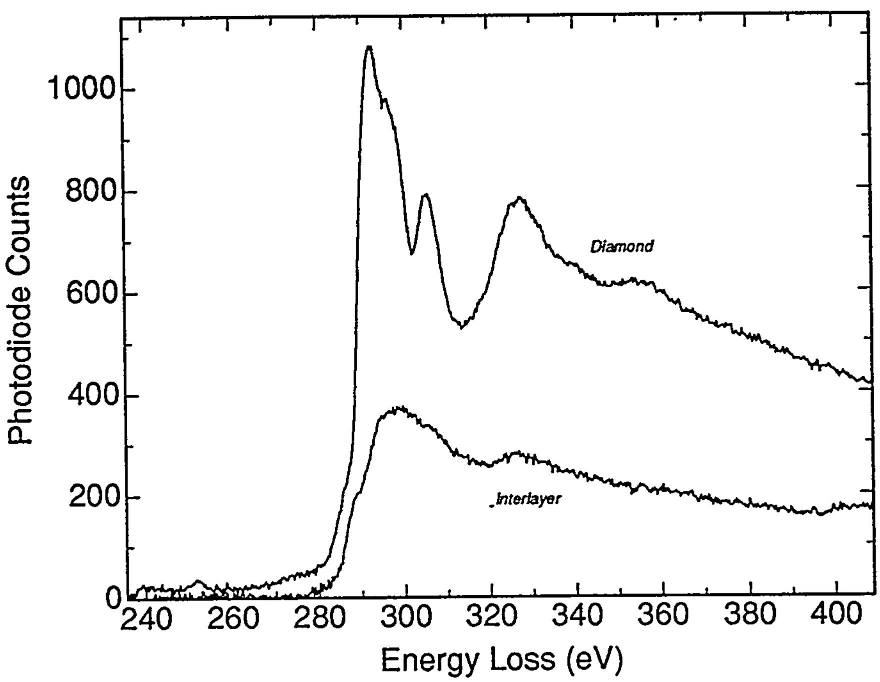

Fig. 5. The carbon k-edge EELS spectra collected from the diamond film and the amorphous interlayer shown in Fig. 4.

CONCLUSIONS

Diamond films grown from fullerene precursors consist of small (15 nm) randomly oriented equiaxed grains. Diamond films grown from methane in argon plasma consist of dendritic grains as well as small randomly oriented equiaxed grains. It is the dendritic microstructure of the methane/argon diamond films that probably results in greater surface roughness as compared to the films grown from fullerene precursors.

The first diamond grains that nucleate from fullerene precursors generally do so on a thin (0.5-20 nm) amorphous carbon interlayer and seldom directly on the silicon substrate. There is also diamond growth on the diamond residue from the scratching pretreatment.

In diamond films grown from fullerene precursors neither columnar nor dendritic grains are observed. Evidently there is continuous nucleation of equiaxed grains throughout the thickness of the deposited film. It is this microstructure of small equiaxed grains throughout the film thickness that is responsible for the very smooth surfaces of diamond films grown from fullerene precursors.

ACKNOWLEDGMENTS

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