Diamond and Related Materials, 2 (1993) 225–228

Characterization of catalytically synthesized turbostratic carbon films used for improved rates of diamond nucleation

Baybars Oral
Max-Planck-Institut für Metallforschung, Institut für Werkstoffwissenschaft, Seestrasse 92, D-7000 Stuttgart 1 (Germany)

Müzeyyen Ece
Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, D-7000 Stuttgart 80 (Germany)

Thierry Rogelet and Zhi Ming Yu
Royal Institute of Technology, Materials Science, Teknikringen 14, S-100 44 Stockholm (Sweden)

Abstract

Turbostratic carbon (TC) films pre-deposited onto copper substrates cause extremely rapid nucleation of diamond when heated in the presence of atomic hydrogen at approximately 1273 K. Transmission electron microscopy and diffraction, Auger electron spectroscopy, and atomic force microscopy were used to characterize the catalytically synthesized TC films. Fine structure analyses in the vicinity of the primary carbon KLL Auger peak showed that the electronic structure of the TC films resembled that of graphite, indicating that the majority of carbon bonding was of sp^2 type. By heating in the presence of atomic hydrogen, the Auger fine structure changed towards the fine structure of diamond. The results are discussed in terms of the formation of stable sp^3 bonding caused by atomic hydrogen.

1. Introduction

Nucleation mechanisms of crystalline diamond on non-diamond substrates are not yet clearly understood. However, it has been widely accepted that the rate of nucleation can be increased by (a) scratching and/or (b) seeding the surface of the substrate with very fine diamond crystals [1]. In addition to these two surface pretreatments, it has also been shown that the nucleation rate can be improved if a thin layer of non-diamond (amorphous or diamond-like) carbon film is deposited onto a substrate prior to diamond growth [2–4].

Recently, Oral and Flodström showed using Raman spectroscopy that diamond crystallites could be formed rapidly (in approximately 1 min) from a catalytically synthesized and highly disordered carbon film [5]. This particular carbon film was defined as a precursor to diamond. Although Raman spectroscopy provided information on the types of carbon bonding, further characterization was needed to identify the crystallographic and electronic structure. In this manuscript, we report the results of transmission electron microscopy and diffraction (TEM and TED), Auger electron spectroscopy (AES), and atomic force microscopy (AFM). The results are discussed in terms of the formation of very small sp^3 bonded crystalline clusters, *i.e.* diamond, as nuclei with the help of atomic hydrogen.

2. Experimental details

The method for preparation of the highly disordered carbon and diamond films will be described here briefly since it has already been described elsewhere [5]. A conventional hot-filament chemical vapor deposition (HFCVD) technique was used to grow the films on polycrystalline copper substrates. However, the technique was slightly modified for growth of the highly disordered carbon films by placing a catalytically active metal sheet (molybdenum, tungsten or tantalum) under the substrate. The carbon film was grown on the surface of the copper substrate facing the catalyst sheet (not on the surface of the substrate facing the two rhenium filaments). After growth of the carbon film, the copper substrate was inverted so that its carbon-coated surface faced the filaments for the following diamond formation process.

During the disordered carbon growth and diamond formation experiments the CH_4-to-H_2 ratios were 0.7:100 and 0.3:100 respectively. The substrate was radiatively heated by the filaments and substrate temperatures were approximately 923 K during the disordered carbon growth and 1273 K during diamond formation. The filament temperature was approximately 2073 K in both cases as measured by an optical pyrometer.

Films were removed from their substrates for the TEM–TED and AFM but kept on the substrate for

0925-9635/93/$6.00

AES. A JEOL 200 CX electron microscope was used for the TEM and TED investigations. The carbon film was thinned using a standard argon ion milling technique with 6 kV accelerating voltage.

AES experiments were performed in an ultrahigh vacuum chamber with a base pressure of 1×10^{-7} Pa (7×10^{-10} Torr) using a Perkin–Elmer Physical Electronics electron gun and cylindrical mirror analyzer. Samples prepared in the HFCVD chamber were taken out into air prior to being mounted on a sample holder carrousel. The Auger electron specra were taken in the differentiated mode with a modulation voltage of 2 V peak-to-peak. The incident electron beam voltage and current used were 2.5 kV and 2.5 mA respectively.

The surface topography of the films was examined with a NanoScope II atomic force microscope. The microscope has a very sharp tip, a few atoms wide at the end, attached to a microcantilever arm on the order of 100–200 μm long. The tip is brought into contact with a sample and is scanned across the surface. An optical system is used to detect the vertical motion of the microtip by sensing the deflection of a laser beam reflected off the back of the tip-supporting cantilever with a two-segment photodiode. Areas of interest on the films were selected with an optical microscope, and then AFM images were obtained in the constant height mode.

3. Results and discussion

One of the highly disordered carbon structures is known as turbostratic carbon (TC). Structurally, a TC cluster is similar to graphite, *i.e.* it consists of hexagonal planes of carbon bonded to each other by sp^2 bonds [6, 7]. However, in contrast to graphite, the basal planes in a TC cluster are rotated in a random manner around the *c*-axis. This rotation modifies the known ...ABAB... stacking sequence of graphite and makes it random. Consequently, the average spacing between the basal planes in the cluster (0.344 nm) is larger than that in graphite (0.335 nm) [6, 7]. In the bulk form, a mean layer diameter of a TC cluster L^a is of the order of 10–15 nm. Usually, $L_c < L_a < 2L_c$ where L_c is the mean height of the clusters [7, 8].

A TEM bright field image and a TED pattern of the highly disordered carbon are shown in Figs. 1(a) and 1(b) respectively. The image shows the typical structure of TC [6]. The two rings marked 10 and 11 in the TED pattern (Fig. 1(b)) are due to electron diffraction from the randomly distributed TC clusters. These diffraction rings are diffused owing to the randomly rotated basal planes of TC clusters. The clusters also contribute to the inner diffuse ring, marked 0002, when the electron beam is perpendicular to their basal planes. For a detailed discussion of the electron diffraction pattern of TC, the reader is referred to the work of Ning *et al.* [6].

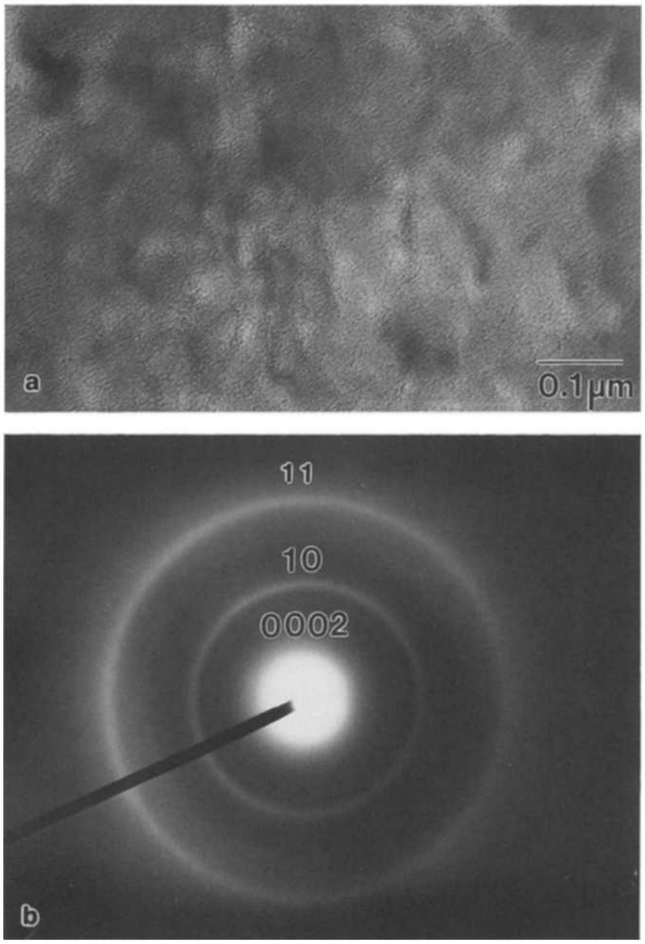

Fig. 1. (a) A TEM bright field image and (b) a TED pattern of turbostratic carbon.

Thin films of medium-range order amorphous carbon (regardless of its hydrogen content) are also believed to be formed from graphitic clusters, *i.e.* clusters of carbon atoms with sp^2-type orbital, if the carbon is deposited at low substrate temperatures [9–11]. Annealing the amorphous carbon at temperatures higher than 875 K in non-oxidizing atmospheres causes growth of these TC clusters [12]. At higher temperatures, the disorder decreases further because of an increase in the level of graphitization, and it continues until complete graphitization is reached (2775 K). Therefore, at temperatures lower than the complete graphitization temperature, TC forms [7], as is seen in our TEM–TED results.

AES fine structure analyses were performed for this TC before and after heat treatment of the film. The AES fine structure of the C KLL peak before heat treatment shows a clear indication of sp^2-type bonding, Fig. 2(a), when compared with previously published AES fine structure of standard graphite [4, 13, 14]. In particular,

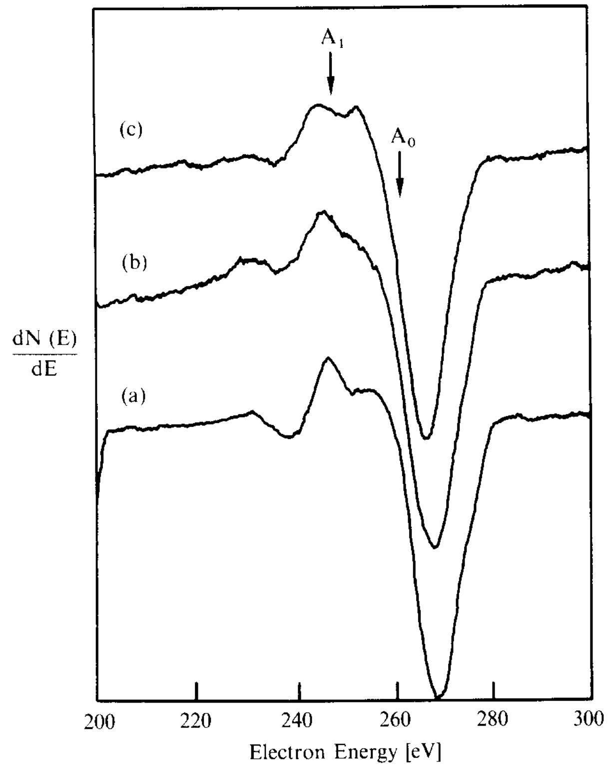

Fig. 2. AES fine structure of (a) turbostratic carbon before any heat treatment, (b) after 1 min heating, (c) after 10 min heating in the presence of atomic hydrogen.

the fine structure intensity of the primary C KLL peak (marked A_0) is smaller than that of the peak located at a slightly lower energy (marked A_1). This result confirms that the bonding in TC is dominantly sp^2-type as in graphite.

The TC film showed a different AES fine structure after being heated in the presence of atomic hydrogen and hydrocarbon radicals for 1 min (Fig. 2(b)). The fine structure in this case was similar to that of evaporated carbon reported by Lurie and Wilson [13]. We interpreted the change in the shape of the AES fine structure as an increase in the proportion of sp^3-type bonding since Raman spectroscopy of the same film (as reported earlier [5]) had also shown a distinct 1332 cm^{-1} diamond peak superimposed on the disorder of graphitic carbon (D-peak) indicating a mixture of sp^2 and sp^3 bonding.

AES taken after 10 min of heating of TC showed the fine structure of diamond (Fig. 2(c)) similar to that reported by Lurie and Wilson [13]. In this case, the intensity of the primary C KLL peak (A_0) increased significantly, indicating the carbon bonding was mainly sp^3-type as in diamond. Not only did Auger fine structure change but also the energy of the primary C KLL peak (268 eV) shifted to lower energies by approximately 2 eV. This shift was attributed to the insulating behavior of diamond [13]. These AES results are in perfect agreement with the results of Raman spectroscopy which had shown a sharp 1332 cm^{-1} diamond peak after the same heat treatment of TC [5].

The surface topography of TC and diamond films was studied with AFM. The surface of the TC film was relatively flat. The waviness h_w (measured as the average distance between the crest and the bottom of major peaks [15]) was approximately 90 nm with a wavelength λ_w of approximately 2000 nm. The roughness of this film, however, was on the submicrometer scale with $h_r \approx 20$ nm and $\lambda_r \approx 250$ nm, Fig. 3(a), where h_r and λ_r are the height and wavelength of the roughness respectively.

The diamond film used for the AFM study was grown on the TC-deposited copper substrates for 100 min. The surface of this film (Fig. 3(b)) was relatively flat ($h_r \approx 150$ nm and $\lambda_r \approx 450$ nm) when compared with our diamond films grown on scratched single-crystal silicon substrates ($h_r \approx 800$ nm and $\lambda_r \approx 2000$ nm) [16]. The high nucleation density was obvious from the topography of the surface of the diamond film (Fig. 3(b)). The number density of crystal aggregates (approximately 3×10^8 crystals cm^{-2}) was approximately two orders of magnitude more than that reported (approximately 2×10^6 crystals cm^{-2}) by Ravi *et al.* [4] where a thin diamond-like carbon film was deposited onto molybdenum to enhance the diamond nucleation rate.

AFM of the back side (against the substrate) of the same diamond film (Fig. 3(c)) showed a very similar topography ($h_w \approx 65$ nm, $\lambda_w \approx 3000$ nm and $h_r \approx 50$ nm, $\lambda_r \approx 325$ nm) to that of the surface of the TC film (Fig. 3(a)). Raman spectroscopy of this surface of the diamond film had also given only the diamond 1332 cm^{-1} peak showing that there was no TC left [5]. The similarity in topographies of the two surfaces along with the results of Raman spectroscopy indicated that the diamond nuclei were initiated from the TC film.

Our present results together with the previously published Raman spectroscopy data [5] indicate that the TC film on the copper substrate helps increase the diamond nucleation rate significantly, hence eliminating the incubation time. We propose the following model to explain the increased diamond nucleation rate. The mainly sp^2-bonded TC films contain a small amount of sp^3-type bonding interconnecting the turbostratic clusters [9]. During heat treatment, these local sp^3-bonded regions become isolated through etching of the sp^2-bonded clusters by atomic hydrogen since the reactivity of the atomic hydrogen with sp^2-bonded carbon is much faster [17, 18]. At the same time, these regions are enlarged owing to the increase in the population of sp^3-bonded carbon with the help of atomic hydrogen [19]. These sp^3-bonded clusters not only become isolated and enlarged but also transform into crystalline diamond of a detectable size (as indicated by the sharpness of the diamond Raman peak since a sharp diamond peak can only be observed when the crystallites reach a critical

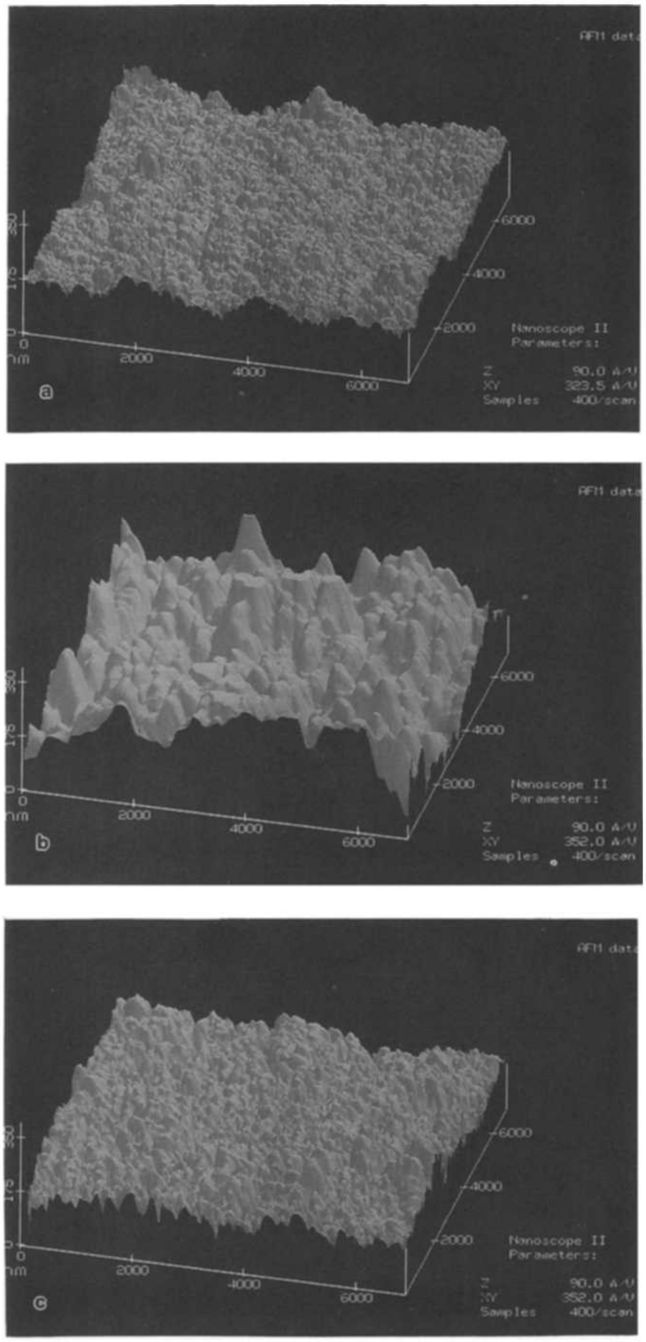

Fig. 3. AFM images of (a) the surface of the turbostratic carbon film, (b) the surface of the diamond film, (c) the back surface of the diamond film in (b).

size [20, 21]) at this heat treatment temperature (approximately 1273 K). In addition, a local increase in the hydrocarbon concentration during the hydrogen etching reaction may also have some effect on the growth of the nuclei but there is no result suggesting that it helps increase the nucleation rate of diamond.

4. Conclusions

The TEM–TED and the AES studies showed that the highly disordered carbon film which was catalytically deposited onto the copper substrate was the type known as turbostratic carbon.

AES results agreed with the previously reported Raman spectroscopy results and showed that diamond nucleated to form crystallites within the first minute of heating of the TC film in an atomic hydrogen rich environment.

The diamond film grown on the TC-deposited copper substrate had a very high density of diamond crystallites which, in turn, caused flatter films.

A proposed model stated that diamond nucleation took place owing to the rapid formation of sp^3-bonded carbon clusters (at the expense of the sp^2-bonded TC clusters) with the help of atomic hydrogen. These sp^3-bonded clusters simultaneously crystallized to form diamond nuclei at around 1273 K.

Acknowledgments

This research was supported by the Swedish Natural Science Research Council and Max-Planck-Gesellschaft.

References

1 W. A. Yarbrough, A. Inspektor and R. Messier, *Mater. Sci. Forum, 52–53* (1989) 151.
2 A. A. Morrish and P. E. Pehrsson, *Appl. Phys. Lett., 59*(4) (1991) 417.
3 J. J. Dubray, C. G. Pantano, N. Meloncelli and E. Bertran, *J. Vac. Sci. Technol., A, 9*(6) (1991) 3012.
4 K. V. Ravi, C. A. Koch, H. S. Hu and A. Joshi, *J. Mater. Res., 5*(11) (1990) 2356.
5 B. Oral and A. Flodström, *Surf. Coat. Technol., 55* (1992) 374.
6 X. J. Ning, P. Pirouz, K. P. D. Lagerlof and J. DiCarlo, *J. Mater. Res., 5*(12) (1990) 2865.
7 I. L. Spain, in P. L. Walker and P. A. Thrower (eds.), *Chemistry and Physics of Carbon*, Vol. 16, Marcel Dekker, New York, 1981, p.119.
8 D. B. Fischbach, in P. L. Walker and P. A. Thrower (eds.), *Chemistry and Physics of Carbon*, Vol. 7 Marcel Dekker, New York, 1971, p.1.
9 J. Robertson and E. P. O'Reilly, *Phys. Rev. B, 35*(6) (1987) 2946.
10 M. A. Tamor, J. A. Haire, C. H. Wu and K. C. Hass, *Appl. Phys. Lett., 54*(2) (1989) 123.
11 M. Yoshikava, G. Katagiri, H. Ishida, A. Ishitani and T. Akamatsu, *Solid State Commun., 66*(11) (1988) 1177.
12 R. O. Dillon, J. Woollam and V. Katkanant, *Phys. Rev. B., 29*(6) (1984) 3482.
13 P. G. Lurie and J. M. Wilson, *Surf. Sci., 65* (1977) 476.
14 B. E. Williams and T. J. Glass, *J. Mater. Res., 4*(2) (1989) 373.
15 D. S. Campbell, in L. I. Maissel and R. Glang, (eds.), *Handbook of Thin Film Technology*, McGraw-Hill, New York, 1983 p.6–14.
16 M. Ece, *Personal communications*; 1992.
17 N. Setaka, *J. Mater. Res., 4*(3) (1989) 664.
18 N. Uchida, T. Kuritak, K. Uematsu and K. Saito, *J. Mater. Sci. Lett., 9* (1990) 251.
19 Y. Wang, H. Chen, R. W. Hoffman and J. Angus, *J. Mater. Res., 5*(11) (1990) 2378.
20 C. B. Collins, F. Davanloo, D. R. Jander, T. J. Lee, H. Park and J. H. You, *J. Appl. Phys., 69*(11) (1991) 7862.
21 J. Robertson, *Prog. Solid State Chem., 21* (1991) 199.