ANL/CHM/CP-98669

GRAIN BOUNDARIES AND MECHANICAL PROPERTIES OF
NANOCRYSTALLINE DIAMOND FILMS*

Hans-Gerd Busmann¹, Antje Pageler¹, Ulf Brauneck², and Dieter M. Gruen³

RECEIVED
OCT 19 1999
OSTI

¹Fraunhofer-IFAM, Bremen, Germany

²Schott Glas, Weisbaden, Germany

³Materials Science and Chemistry Divisions, Argonne National Laboratory, Argonne, IL 60439

submitted for presentation at and for the proceedings of the

International Symposium on Metastable, Mechanically Alloyed and Nanocrystalline Materials 1999
(ISMANAM-99)

Dresden, Germany

August 30-September 3, 1999

The submitted manuscript has been created by the University of Chicago as Operator of Argonne National Laboratory ("Argonne") under Contract No. W-31-109-ENG-38 with the U.S. Department of Energy. The U.S. Government retains for itself, and others acting on its behalf, a paid-up, nonexclusive, irrevocable worldwide license in said article to reproduce, prepare derivative works, distribute copies to the public, and perform publicly and display publicly, by or on behalf of the Government.

*Work supported by the U.S. Department of Energy, BES-Materials Sciences, under Contract W-31-109-ENG-38.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, make any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

**Portions of this document may be illegible
in electronic image products. Images are
produced from the best available original
document.**

GRAIN BOUNDARIES AND MECHANICAL PROPERTIES OF NANOCRYSTALLINE DIAMOND FILMS

Hans-Gerd Busmann^a, Antje Pageler^a, Ulf Brauneck^b and Dieter M. Gruen^c

^aFraunhofer-IFAM, Wiener Str. 12, D-28359 Bremen, Germany

^bSchott Glas, Hagenauer Str. 38, 65203 Wiesbaden, Germany

^cMaterials Science and Chemistry Divisions, Argonne National Laboratory, Argonne, IL 60439, USA

KEYWORDS: Nanocrystalline Diamond, Grain Boundaries, Hardness

ABSTRACT

Phase-pure nanocrystalline diamond thin films grown from plasmas of a hydrogen-poor carbon argon gas mixture have been analyzed regarding their hardness and elastic moduli by means of a microindenter and a scanning acoustic microscope. The films are superhard and the moduli rival single crystal diamond. In addition, Raman spectroscopy with an excitation wavelength of 1064 nm shows a peak at 1438 1/cm and no peak above 1500 1/cm, and X-ray photoelectron spectroscopy a shake-up loss at 4,2 eV. This gives strong evidence for the existence of solitary double bonds in the films. The hardness and elasticity of the films then are explained by the assumption, that the solitary double bonds interconnect the nanocrystals in the films, leading to an intergrain boundary adhesion of similar strength as the intragrain diamond cohesion. The results are in good agreement with recent simulations of high-energy grain boundaries.

INTRODUCTION

Perfect crystal diamond has outstanding properties such as hardness, optical transparency, and thermal conductivity. It is thus an attractive material for many applications. Plasma-assisted chemical vapor deposition (PACVD) is now widely used for the development of commercial uses of diamond thin films for tools, diaphragm, heat sinks, surface acoustic wave devices, and optical windows. Deviations of the properties of PACVD diamond films from those of perfect crystal diamond are mainly due to the microstructure of the films. Thus, the columnar grain structure and grain boundaries extending through the films tend to decrease hardness, optical transparency and thermal conductivity. Conventional diamond PACVD processes involve the use of hydrocarbon / hydrogen plasmas with a large excess of hydrogen (typically 99%). The presence of large amounts of hydrogen is frequently cited to be mandatory for diamond vapor growth because hydrogen is said to stabilize surface radical sites thereby preventing graphitization.

Recently a new type of microwave plasma chemistry has led to phase-pure nanocrystalline diamond (PPNCD) films with a densely packaged diamond grains with diameters between 3 nm and 20 nm [1,2]. The gas phase contains argon (~ 100 mbar), either fullerenes ($\sim 10^{-2}$ mbar) or methane (~ 1 mbar), and about 1 mbar hydrogen. The small amount of hydrogen tends to stabilize the plasma and has only minor effects on the properties of the films. PPNCD deposition from a fullerene / argon mixture entirely without added hydrogen has been demonstrated [3]. One main difference of this type of plasma as compared to hydrogen-rich diamond PACVD is a high renucleation rate for new diamond crystals [4], which cause the nanograin structure. Deposition of PPNCD is performed in conventional microwave plasma systems for diamond PACVD. Proof of phase-purity was given by a variety of characterization methods including electron energy loss spectroscopy. The percentage of non- sp^3 bonded C-atoms has been estimated to be between 3% and 10% reflecting the presence of π -bonded carbon at the grain boundaries [5].

Fig. 1: Microindenter load – displacement curves of a synthetic IIB diamond (Sumitomo), a phase-pure nanocrystalline diamond (PPNCD) film (thickness 3 μm) and a silicon (100) wafer.

H by using the definition $H = P / (26.43 h^2)$ is not possible, even if the "indentation size effect" is considered [7,8]. Fig. 3 shows as-measured load-displacement curves of a nanocrystalline thin film grown from the $\text{CH}_4/\text{H}_2/\text{Ar}$ gas mixture in comparison to a synthetic diamond(100) and silicon(100). The maximal load is 25 mN for all samples, yielding indentation depths of 116 nm, 102 nm, and 250 nm, respectively. All curves are the average of at least ten single measurements, however, scattering among them is very low. The elastic hardness of the PPNCD film is 78% of that of the synthetic diamond, assuming that the hardness is proportional to $1/h^2$. The film is thus superhard and fully elastic carbon. For comparison, the silicon sample in Fig. 1 exhibits strong plastic deformation and a displacement discontinuity below a loading of 10 mN, superhard carbon nitride thin films already exhibit a substantial plastic behavior at a loading of 5 mN [9] and single crystalline (0001) Sapphire exhibits displacement discontinuities already below a loading of 15 mN [10].

The PPNCD film shows the same total elastic recovery as the single crystalline diamond, i.e., the curves of penetration and release of the indenter are practically equal. Since the size of the indenter is much larger than the diameter of the individual grains of the nanocrystalline film, this total elasticity clearly demonstrates a high resistance against grain boundary sliding.

ACOUSTIC PROPERTIES

Elastic constants have been studied with a reflection-type scanning acoustic microscope (SAM 2000, KSI) at a fixed frequency of 1 GHz. The film is exposed to a perpendicularly impacting, focused acoustic wave, with the focus being below the surface. At the surface, this wave is partly transformed to a surface acoustic wave (SAW). This SAW backemits a acoustic wave into the space above the surface, where it interferes with the specularly reflected wave. The microscope records the intensity of this interference (piezo-crystal induced voltage V) as a function of the depth z of the focus below the surface [11], yielding V(z) plots. Fig. 2 shows the

PPNCD films show smooth surfaces, low friction coefficients, low wear, and low onset voltages for electron emission. They can be conformally coated on microstructured substrates. Potential applications are fluid pump seals, cold cathodes, microelectro-mechanical systems and machining of difficult-to-cut materials. In this paper, we present data about mechanical, acoustical, vibrational and electrical properties of PPNCD, and these are discussed within the high-energy grain boundary model advanced by Koblinski et al. [6].

MECHANICAL PROPERTIES

Microhardness characterization was performed with a Fisherscope H100 microindenter with which the displacement h of a Vickers-type diamond has been recorded as a function of its load P. The outermost end of the tip of the indenter has a curvature with a radius of about 0.5 μm and an edge length parallel to the substrate of 0.2 μm - 0.5 μm . Thus, the lateral extensions of the indentations are at least a factor of ten larger than the size of the crystallites in the films. The maximal indentation depth h was kept below 10% of the film thickness in order to avoid any influence of the substrate on the indentation. Since this is less than the curvature of the indenter, a qualitative deduction of the hardness

Fig. 2: Measured and simulated $V(z)$ - curve for a 5 μm thick phase-pure nanocrystalline diamond (PPNCD) film as obtained with a scanning acoustical microscope.

Fig. 3: Raman spectra of a synthetic I Ib diamond (Sumitomo), pyrolytic graphite and a 3 μm thick phase-pure nanocrystalline diamond (PPNCD) film. The excitation wavelength was 1064 nm.

interference pattern obtained in this way for a 5 μm thick PPNCD film. It shows a sine-like pattern, and the transversal velocity v_t of the SAW can be calculated from the period of $V(z)$ curve [12] to 10450 m/s.

Young's modulus E and the shear modulus G are related to v_t through the equations $G = \rho v_t^2$ and $E = 2(1+\nu)G$. With the mass density $\rho = 3,51 \text{ g/cm}^3$ and the Poisson's ratio $\nu = 0,107$ of diamond [13], these equations result in $G = 384 \text{ GPa}$ and $E = 864 \text{ GPa}$, which are close to crystal diamond ($G \sim 354 \text{ GPa}$ to 535 GPa , $E \sim 1040 \text{ GPa}$).

VIBRATIONAL PROPERTIES

Raman spectroscopy is widely used for the characterization of diamond thin films because it allows the discrimination between totally sp^3 -bonded carbon, with a narrow phonon peak at 1332 $1/\text{cm}$, and carbon with other bonding configurations and thus different Raman spectra. The relative strength of Raman scattering for differently bonded carbon is also strongly dependent on the excitation wavelength due to electronic resonance effects; enhanced scattering is observed in the case of sp^3 -type bonds with high-energy excitation (UV-light) and in the case of sp^2 -type bonds with low-energy excitation (infrared light). Raman spectra of PPNCD films taken with excitation wavelengths in the visible and UV spectral regime exhibit a sharp phonon peak at 1332 $1/\text{cm}$ and a peak at 1125 $1/\text{cm}$. A peak at about 1125 $1/\text{cm}$ was also observed in nanocrystalline diamond samples grown in a 1% CH_4 / 99% H_2 plasma at low substrate temperature (650 $^\circ\text{C}$) and has been attributed to diamond crystal size effects on the Raman selection rules [14].

Fig. 3 shows Raman spectra taken from PPNCD, graphite powder and I Ib-diamond, taken with a Fourier transform infrared spectrometer (Bruker IFS 66/S - FRA106) and excitation at 1064 nm. Graphite shows the usual phonon peak at 1580 $1/\text{cm}$ and disorder peak at 1285 $1/\text{cm}$, and diamond the already mentioned peak at

Fig. 4: X-ray photoelectron spectrum of a 3 μm thick phase-pure nanocrystalline diamond (PPNCD) film for electron energies in the range of the C1s binding energy.

carbon network, referring to the fact, that the peaks above 1500 $1/\text{cm}$ in graphite and many types of amorphous carbon are due to in-plane vibrations of mostly sp^2 bonded carbon networks (the so-named G-peak). The PPNCD Raman spectrum shown in Fig. 3 is thus consistent with a carbon structure, in which solitary carbon double bonds are embedded in an otherwise sp^3 bonded carbon structure.

ELECTRONIC PROPERTIES

Any deviation from perfect sp^3 bonding should result in electronic states within the diamond band gap. Energy loss spectra of PPNCD samples taken in a high resolution transmission electron microscope did not give evidence for an energy loss feature due to graphitic states [17], however this measurement does not disprove the existence of a small amount of non-diamond carbon. Fig. 4 shows a X-ray excited photoelectron spectrum of a PPNCD film in the binding energy range of C1s electrons, taken with a $\text{Al}_{K\alpha}$ excitation radiation (ESCALAB 220i-XL, Vacuum Generators). The measured data have been corrected with respect to secondary electron emission [18] and thereafter decomposed into a superposition of five Gaussian profiles by means of a Levenberg-Marquardt-algorithm. The main peak at a binding energy of 284,5 eV is due to all-carbon bonded carbon atoms. Its width amounts to 1,1 eV and, since the energy difference between differently hybridized C atoms is $\sim 0,3$ eV [18,19], it is not possible to identify non-diamond C-C bonds in this spectrum. The three peaks with an energy difference (chemical shift) with respect to the C-C peak of 0,95 eV, 1,8 eV and 2,6 eV are due to C-H [20], C-O and C=O [21], respectively. The presence of oxygen in addition to hydrogen is possibly due to the lack of a large excess of hydrogen during growth [22].

The final feature of this spectrum is the peak with an energy difference with respect to the C-C peak of 4.2 eV. Such a high chemical shift of C1 electrons appears only in extremely electronegative bonding situations like N-C-O₂, which are very unlikely for PPNCD. The peak at 4.2 eV is thus most likely due to excitation of C2sp electrons into unfilled electronic states (shake-up loss). The corresponding shake-up loss of graphite is found at 6.3 eV and assigned to $\pi\pi^*$ excitations [23,24]. The energy difference of 4,2 eV is less than the diamond

1332 $1/\text{cm}$. The PPNCD film apparently exhibits a superposition of three contributions: One peak at 1125 $1/\text{cm}$ and a broad hump around 1340 $1/\text{cm}$, that we attribute to scattering by diamond as mentioned before. The third contribution is a peak at 1438 $1/\text{cm}$. Peaks in between the phonon peaks of graphite and diamond are frequently observed in diamond PACVD films, however, they are normally located above 1500 $1/\text{cm}$ and attributed to non-diamond carbon of sp^2 or mixed sp^2/sp^3 hybridization [15]. Yarbrough and Roy [16] reported Raman spectra of nanocrystalline diamond samples grown in a 1% CH_4 / 99% H_2 plasma (see also [14]). For grain sizes below 20 nm, these contain a peak at 1460 $1/\text{cm}$, in addition to peaks above 1500 $1/\text{cm}$. The peak at 1460 $1/\text{cm}$ they attribute to non-crystalline tetrahedrally bound carbon structures. The peak at 1438 $1/\text{cm}$ in the present PPNCD spectrum may thus tentatively be assigned to Raman scattering at a carbon structure that contains sp^2 and sp^3 bonds, however, with an essentially higher sp^3 character than the non-diamond structures in other PACVD diamond films. The absence of peaks at higher energy can be explained by the lack of an almost sp^2 bonded

band gap of 5.2 eV, and the spectrum in Fig. 3 thus gives strong and direct evidence for the presence of electronic states within the diamond band gap, in accord with theoretical calculations [17].

DISCUSSION

The hardness and elastic moduli of PPNCD films rival single crystal diamond, whereas the vibrational and electronic properties exhibit distinct differences. The hardness of nanocrystalline materials is very much determined by their grain boundaries. In metals, when the grain size decreases below 20 nm, a frequently observed softening has been attributed to grain boundary sliding [25], in that grain boundary sliding becomes increasingly easier with decreasing grain size (reverse Hall-Petch effect). In a similar way, grain boundary sliding is also recognized as the dominant mechanism for high-temperature creep in nanocrystalline ceramics [26]. The mechanical properties of the PPNCD films at room temperature as described above imply now, that grain boundary sliding is strongly inhibited even for nanocrystalline grains and that the average intergranular bond of PPNCD is about of equal strength as the intragranular bond of single crystal diamond. This can be explained by covalent carbon bonds crosslinking the grains. The observed vibrational and electronic properties of PPNCD, that is the Raman peak at 1438 $1/\text{cm}$ and the electronic shake-up loss of 4.2 eV, then indicate that the intergranular bonds are at least partly solitary double bonds. Such double bonds would be of higher binding energy than single bonds characteristic of the intragranular bonds. However, the grain boundary area specific density could be lower than the intragranular bond density, such that in total the adhesive grain boundary energy is similar to the cohesive energy of single crystal diamond.

The occurrence of double bonds in the grain boundaries is comprehensible owing to a proposed C_2 nucleation mechanism. The mechanism involves insertion of C_2 groups into the π -bonds of dimer rows of a reconstructed (100) surface. Total densities of states for both a π -bonded (double bonded) stacking fault and a $\Sigma 5$ twinned grain boundary have been calculated using periodic density functional methods [17].

Until now there are no experimental indications that the relative crystallographic orientation of two adjacent grains in PPNCD show any orientational preferences, nor are there models to favor preferred orientations on the basis of energetic or molecular-kinetic considerations. Considering the large manifold of incommensurate and large-unit-cell grain boundaries of diamond, Koblinski et al. [6,27] show, that high-angle twist boundaries of (100) planes are representatives for this manifold: The (111) and (110) twist boundaries are unique in that only 25% of the interface bonds involve atoms across the interface; all others including the (100) twist boundaries involve 50%. According to their Monte-Carlo simulations, this has the consequence, that high-angle (100) twist boundaries are of higher stability than corresponding (111) and (110) boundaries due to the relatively large number of sp^2 bonds connecting the grains in the (100) twist boundary. In principle, such high-energy grain boundaries can be mechanically stronger than even the perfect crystal. This result nicely explains the experimentally obtained high hardness and elastic constants as described above.

The consonance between these simulations and the present experimental work is even more striking, if we now consider the vibrational and electronic properties. According to the simulations, the sp^2 coordinated atoms are rather poorly connected amongst themselves, thereby preventing the formation of graphite-like structures [6], in agreement with the observed Raman peak at 1438 $1/\text{cm}$ and the lack of peaks above 1500 $1/\text{cm}$. The local electronic density of a diamond (100) $\Sigma 29$ grain boundary as obtained from the simulation [27] show that the bonds in between the interface form a mixture of sp^2 and sp^3 bonds with electronic states within the diamond band gap. Considering, that only 3% - 10% of all carbon atoms are involved in the grain boundaries, the shake-up loss of 4.2 eV can be due to an excitation of an electron out of a filled interface state into an unfilled interface state, or more likely, between interface states and states of the diamond crystals.

In summary, this work shows that the hardness and elastic properties of PPNCD rival single crystal diamond. In addition, those vibrational and electronic properties that are different from single crystal diamond are attributed to high energy grain boundaries with strong sp^2 bonds connecting the grains. The experimental data are in good agreement with reported Monte-Carlo grain boundary simulations.

ACKNOWLEDGEMENT

Sincere thanks are due to A. Steffen for his assistance for the microhardness measurements. The work supported by the German "Bundesministerium fuer Bildung, Wissenschaft, Forschung und Technology" (BMBF) under Contract No. 13N6630/9 and the State of Bremen under the auspices of the research program "Preparation, Properties and Reliability of Microstructured Composite Materials"; and by the U.S. Department of Energy, BES-Materials Sciences, under Contract W-31-109-ENG-38.

REFERENCES

- [1] D.M. Gruen, S.Liu, A.R. Krauss, J. Luo and X.Pan, *Appl. Phys.Lett.* 64 (1994), p. 1504.
- [2] D.M. Gruen, C.D. Zuiker, A.R. Krauss, and X.Pan, *J.Vac.Sci.Technol.* 13 (1995), p. 1628.
- [3] H.-G. Busmann, U. Brauneck, H.-W. David, S. Diekhoff, and S. Boseck, in *Proc. XI. Int. Winterschool on Electronic Properties of Novel Materials – Molecular Nanostructures*, Eds. H. Kuzmany, J. Fink, M. Mehring and S. Roth, World Scientific Publishing Company, 1998, p. 500-505.
- [4] D. Zhou, A.R.Krauss, T.D. Corrigan, T.G.McCauly, R.P.H. Chang, and D.M. Gruen, *J.Electrochem. Soc.* 144,8 (1997), p. L224.
- [5] L.C. Qin, D. Zhou, A.R. Krauss and D.M. Gruen, *Nanostructured Materials* 10 (1998), p. 649.
- [6] P. Koblinski, D. Wolf, S.R. Phillpot, H. Gleiter, *J. Mater. Res.* 13,8 (1998), p. 2077.
- [7] M.F. Doerner, W.D. Nix, *J. Mater. Res.* 1 (1986), p. 601.
- [8] H.-H. Behncke, *Härtereitechnische Mitteilungen, Zeitschrift für Wärmebehandlungen und Werkstofftechnik*, 48,5 (1993).
- [9] S. Sjöström, S. Stafström, M. Boman, and J.-E. Sundgren, *Phys. Rev. Lett.* 75,7 (1995), p.1336.
- [10] T. Page, W.C. Oliver and C.J. McHargue, *J. Mater. Res.* 7,2 (1992), p. 450.
- [11] Z. Yu, S. Boseck, *Rev. Mod. Phys.* 67,4 (1995), p. 863.
- [12] G.A.D. Briggs, *Acoustic Microscopy*, Clarendon, Oxford, 1992.
- [13] J. E. Field, *Properties of Diamond*, Academic Press, New York, 1993.
- [14] W.A. Yarbrough and R. Messier, *Science* 247 (1990), p. 688.
- [15] C. Wild, N. Herres, J. Wagner, P.Koidl, T.R. Anthony, *Proc. 1st Int. Symp. on Diamond and Diamond-Like Films*, Eds. J.P. Dismukes et al., The Electrochemical Society, Pennington, NJ, 1989, p. 283-295.
- [16] W.A. Yarbrough and R. Roy, in *Diamond and Diamond-Like Materials Synthesis*, Eds. G.H. Johnson, A.R. Badzian, M.W. Geis, Materials Research Society, Pittsburgh, PA, 1988, p.33.
- [17] P. Zapol, L.A. Curtiss and D.M. Gruen, *Mat. Res. Soc. Symp. Proc. Vol. 538* (1999), p. 371.
- [18] J.F. Morar, F.J. Himpsel, G. Hollinger, J.L. Jordan, G. Hughes, F.R. Feeley, *Phys. Rev. B* 33,2 (1986), p. 1340.
- [19] S.C. Sharma, M. Green, R.C. Hyer, C.A. Dark, T.D. Black, A.R. Chourasia, D.R. Chopra, K.K. Mishra, *J. Mater. Res.* 5,11 (1990), p. 2424.
- [20] B.B. Pate, *Surf. Sci.* 165 (1986), p. 83.
- [21] *High Resolution XPS of Organic Polymers*, The Scientific ESCA 300 Database, John Wiley & Sons.
- [22] H.-G. Busmann, U. Brauneck, and H.-W. David, *Carbon* 36 (1998), p. 529.
- [23] S.R. Kasi, H. Hang, J.W. Rabalais, *J. Vac. Sci. Technol. A* 6 (1988), p. 1788.
- [24] D. Ugolini, J. Eitle, P. Oelhafen, *J. Appl. Phys.* A54 (1992), p. 57-60.
- [25] J. Schiotz, F.D. Di Tolla, K.W. Jacobsen, *Nature*, 391 (1998), p. 561.
- [26] *Nanomaterials: Synthesis, Properties and Applications*, Eds. A.S. Edelstein, R.C. Cammarata, Institute of Physics Publishing, Bristol and Philadelphia, 1996.
- [27] P. Koblinski, D. Wolf, F. Cleri, S.R. Phillpot, H. Gleiter, *MRS Bulletin*, 23,9 (1998), p. 36.