DETERMINATION OF ELASTIC AND MECHANICAL PROPERTIES OF NANOCRYSTALLINE SUPERHARD MATERIALS BY LASER ULTRASONICS

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Abstract

The Young's modulus and density of low-pressure-synthesized superhard thin films of diamond and cubic boron nitride with column diameters in the nano- to micrometer range were measured by the surface acoustic wave technique. The elastic and mechanical properties of the films are compared with the corresponding single-crystal values.

Introduction

Nanophase materials may have strongly grain-size-dependent linear and nonlinear elastic and mechanical properties. Especially in covalent superhard materials, such as diamond and cubic boron nitride (cBN), usually the density, elastic moduli, hardness, and fracture strength deteriorate with decreasing grain size, because the grain boundaries possess a lower density, stiffness, hardness, and bonding strength than the single-crystal lattice. It is very important to investigate the nature of these grain boundaries for different deposition methods and various growth conditions. A practical reason to optimize the properties of these materials is the reduction of the intrinsic surface roughness of the nanocrystalline films, which may be used as hard and resistant coatings, since polishing is both difficult and expensive.

Experimental

The dispersion effect in laser-excited surface acoustic wave (SAW) pulses propagating along the surface of a film-substrate system was monitored with a contact piezoelectric PVDF-foil transducer [1]. With this detector frequencies up to 300 MHz can be recorded and optical quality of the surface is not required as in contact-free optical detection techniques [2]. The anomalous dispersion of the phase velocity, usually observed in superhard films, was calculated from the SAW profiles measured at two distances from the thermoelastic source. The resulting dispersion curves were fitted by theory, assuming the films to be isotropic layers on an anisotropic silicon substrate, to extract the film properties [3]. A large contrast between the acoustic properties of the film and substrate coupled with a sufficient film thickness lead to a characteristic nonlinear dispersion curve and allows the accurate determination of up to three film properties, if the corresponding substrate properties are known.

The density, Young's modulus, and Poisson's ratio of the nanocrystalline columnar-structured CVD-diamond and cBN films, with submicrometer column diameters and thicknesses between several hundred nanometers and several micrometers were fitted. With the SAW method mean values of the density and the Young's modulus or stiffness, averaged over the macroscopic SAW propagation distances, were obtained for the graded superhard films with grain diameters normally changing from the nucleation side to the growth side. Accordingly the method provides an overall macroscopic quality control of the film quality.

Results and discussion: diamond

Nanocrystalline columnar-structured diamond films with mean column diameters less than 100 nm and thicknesses in the range of 1-5 μm were grown on silicon substrates by chemical vapor deposition (CVD) in a microwave plasma reactor with purified methane and hydrogen used as the reactants. Uniform conformal nucleation densities in excess of 10^{12} cm^{-2} were accomplished prior to growth by seeding with explosively formed nanodiamonds, resulting in good optical quality films [4].

The diamond film properties were studied for very different and not always well known nucleation densities. For diamond films grown with a low nucleation density of $<10^{10}$ cm^{-2} the stiffness was in the range 500-550 GPa, which is only about half the theoretical value of 1143 GPa calculated for ideal polycrystalline diamond, whereas at nucleation densities $>10^{12}$ cm^{-2} Young's moduli of 1120 GPa were found, approaching the ideal value. This high stiffness indicates exceptionally high-quality grain boundaries in these samples.

In Fig.1 results obtained for CVD diamond by the SAW method for the densities and Young's moduli are collected, including results reported for microcrystalline films [3], nano-crystalline films and plates [4], and polycrystalline diamond plates [5]. To judge the quality of the CVD material the results should be compared with the properties of single-crystal diamond. It becomes evident that the stiffness

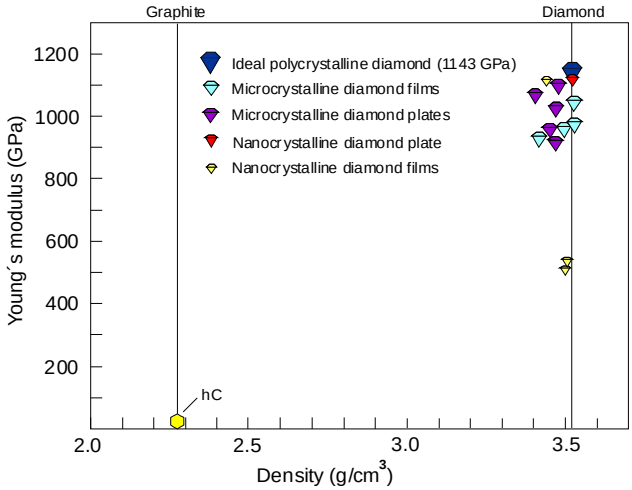

Fig. 1: Young's modulus versus density for nano- and microcrystalline CVD diamond films and plates.

varies considerably. This can be connected with the extent and nature of the interface layer and with the quality of the grain boundaries. In addition, the nucleation and interface layer may lead to a pronounced dependence of the mechanical properties on the film thickness, especially for submicrometer films.

Bonding information was extracted by micro-Raman and photoluminescence measurements (Fig. 2a,b)). The analysis indicates that a higher nucleation density during growth leads to more rapid film coalescence and thus less volume of voids, amorphous, or sp^2-bonded carbon in the nucleation layer, and early stages of film growth (~10-100 nm). This in turn may impact the strength or degree of amorphous carbon extending into the grain boundaries. In fact, as shown in Fig. 2a), slightly more sp^2 and amorphous carbon is present in the low nucleation density material. The grain size and morphology of the diamond films were characterized by scanning electron microscopy (SEM). A comparison of the SEM images on the nucleation side indicates large dark cracks or lines between the nuclei in the film and on the growth surface in the low nucleation density case, as can be seen in Fig. 3a,b). All this suggests that the properties of the grain boundaries and film microstructure, whose evolution depends quite sensitively on the nucleation density, impact the mechanical properties in a dramatic way.

These results clearly demonstrate that a surprisingly high stiffness can be reached in column-structured diamond films with column diameters in the nanometer range. Indeed, these films possess a much flatter surface than the microcrystalline materials. Surprisingly, the corresponding densities were rather independent of the nucleation density and agreed within a few percent with the value of single-crystal diamond. It should be pointed out that the Young's

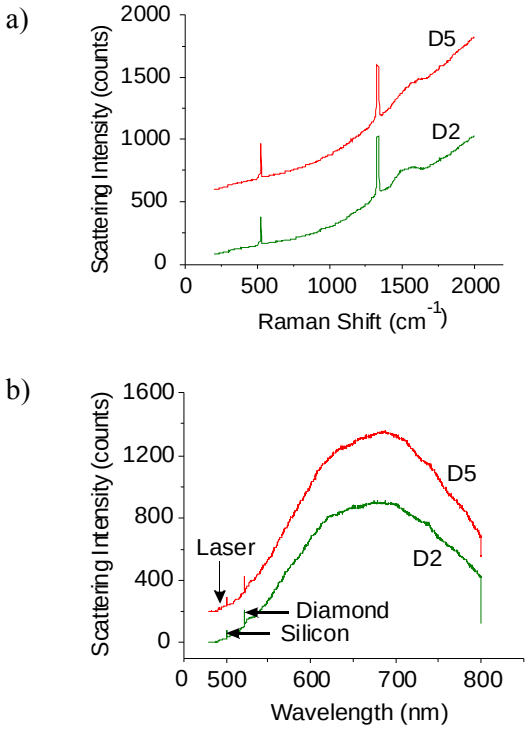

Fig. 2a,b): Micro-Raman spectra a) and photo-luminescence spectra b) of samples D2 and D5 with low and high nucleation density, respectively.

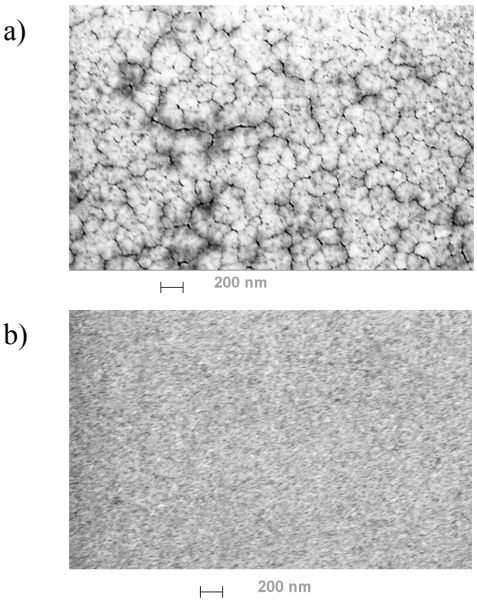

Fig. 3a,b): SEM of a portion of the initial nucleation surfaces a) of film D2 and b) of film D5.

modulus and density are to some extent coupled properties in the present SAW analysis and in this respect the errors involved in their determination by

the SAW technique may be somewhat larger than expected.

Results and discussion: cubic boron nitride

Contrary to the situation encountered with CVD diamond, most of the cBN films deposited up to now mainly by physical vapor deposition (PVD) methods were nanocrystalline with grain sizes in the 10-20 nm range, submicrometer thickness, and a high residual intrinsic stress. Only recently has the deposition of much thicker films with larger grain diameters approaching the micrometer size been realized by a CVD technique [6].

Different methods have been applied to deposit the nanocrystalline cBN samples investigated here, such as ion-assisted pulsed laser deposition and plasma-enhanced physical vapor deposition. These films typically had a thickness of less than 400 nm and contained a 25-50 nm thick buffer layer consisting of hexagonal boron nitride (hBN) to improve adhesion [7]. Since in this case the interface or transition layer represents a substantial fraction of the total film a two-layer method was used to analyze the SAW data, assuming a homogeneous hBN transition layer and a homogeneous cBN layer on an anisotropic silicon substrate [7].

As shown in Fig. 4, the density of the investigated 200-420 nm thick nanocrystalline PVD films varied between 2.95 and 3.35 g/cm^3 and their stiffness between 420 and 505 GPa. As can be also seen in Fig. 4, these values are considerably lower than the corresponding properties of single-crystal cBN, namely 3.49 g/cm^3 and 909 GPa [7]. On the other hand, the 2 µm thick CVD sample with larger grain size had a density of 3.48 g/cm^3 and a Young's modulus of 587 GPa.

The larger deviations of the Young's modulus and density from the single-crystal data in the cBN case can be understood on the basis of a larger influence of the relatively soft transition layer, a lower quality of the grain boundaries, and a pronounced graded film morphology. Up to now elastic properties approaching those of single-crystal cBN could be obtained only with cBN powders sintered at relatively high pressures and temperatures [8], also shown in Fig. 4.

A similar value for the Young's modulus of about 600 GPa can be extracted from microhardness experiments, performed with a Berkovitch diamond indenter, by extrapolation of the experimental results to zero indentation depth ("ultralow-load indenter"). On the other hand, the effective Young's modulus approached the stiffness of the silicon substrate (160 GPa) when the penetration depth of the indenter increased to several hundred nanometers. This is illustrated in Fig. 5, presenting the Young's modulus versus depth for the 2 µm cBN sample [6]. The loading and unloading curves were recorded with the

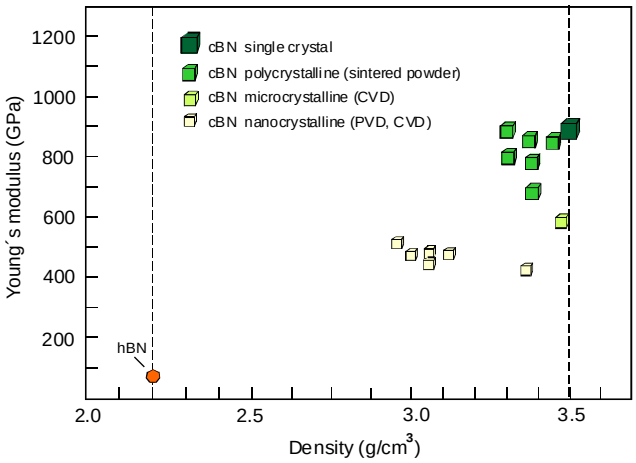

Fig. 4: Young's modulus versus density for nano- and microcrystalline cBN films and sintered powders.

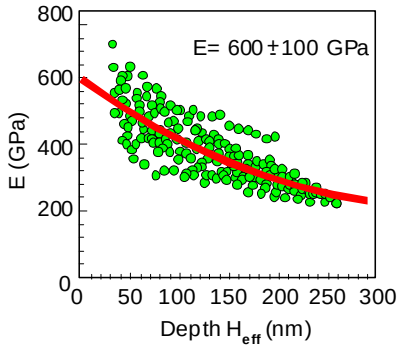

Fig. 5: Young's modulus versus depth curve measured for the 2 µm thick cBN film with the diamond indenter.

Hysitron Triboscope and evaluated according to the Oliver-Pharr model.

It is important to note that for such hard films the measured mechanical film properties may be influenced by the substrate even when the penetration of the indenter is only 3-5% of the film thickness.

The corresponding microhardness of this 2 µm thick submicrocrystalline cBN film was 40 ± 7 GPa, as can be seen in Fig. 6. This is at the lower limit of the hardness range usually defined for superhard materials (40-90 GPa) [9,10]. The large scatter of the data is mainly due to the relatively high surface roughness of 61 nm rms of this film in connection with the low indenter penetration depth.

Cross-sectional TEM micrographs revealed that the structure changed from the nucleation to the growth

side. During nucleation a transition layer of ~100 nm thickness was formed, consisting of nanometer-sized amorphous BN, hBN, and cBN clusters. With increasing thickness, most grains were overgrown or coalesced, forming submicrometer cBN grains at the film surface [6].

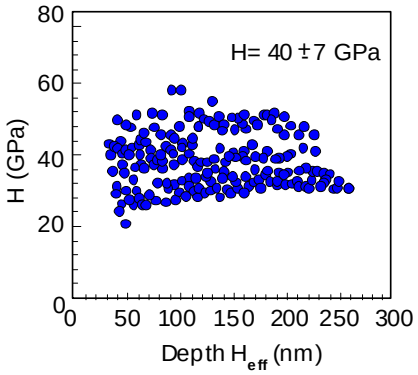

Fig. 6: Microhardness versus depth curve measured for the 2 μm thick cBN film.

Conclusions

Nanocrystalline CVD films of diamond may possess a strongly deteriorated Young's modulus, reaching only about half the single-crystal value. However, under optimized conditions, such as the present high nucleation densities, diamond films with surprisingly high quality grain boundaries could be grown, approaching the stiffness and the density of single-crystal diamond. In addition, the flatness of the surface is considerably improved.

State-of-the-art cBN films, deposited by PVD and CVD methods, exhibit much larger deviations from the single-crystal properties. This is especially true for the effective Young's modulus and density of submicrometer thick nanocrystalline films with a soft hBN transition layer and strongly graded elastic and mechanical properties from the nucleation to the growth side. Films with a Young's modulus and density approaching the values of single-crystal cBN have not been achieved up to now. Since cBN has a hardness of about 70 GPa, as compared to 90 GPa of diamond, and elastic constants coming closest to those of diamond there is growing interest in this material. With respect to its higher oxidation resistance and greater chemical resistance to ferrous alloys, such as steel, cBN is superior to diamond.

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References

[1] A. Lomonosov, A.P. Mayer, and P. Hess, in *Modern Acoustical Techniques for the Measurement of Mechanical Properties*, edited by M. Levy, H.E. Bass, and R. Stern, Vol. 39**,** pp. 65-134, Academic Press, Boston, 2001.

[2] H. Coufal, R. Grygier, P. Hess, and A. Neubrand, "Broadband detection of laser-excited surface acoustic waves by a novel transducer employing ferroelectric polymers," J. Acoust. Soc. Am. 92, pp. 2980-2983, 1992.

[3] R. Kuschnereit, P. Hess, D. Albert, and W. Kulisch, "Density and elastic constants of hot-filament-deposited polycrystalline diamond films: methane concentration dependence," Thin Solid Films 312, pp. 66-72, 1997.

[4] J. Philip, P. Hess, T. Feygelson, J.E. Butler, S. Chattopadhyay, K.H. Chen, and L.C. Chen, "Elastic, mechanical, and thermal properties of nano-crystalline films," J. Appl. Phys. 93, pp. 2164-2171, 2003.

[5] G. Lehmann, M. Schreck, L. Hou, J. Lambers, and P. Hess, "Dispersion of surface acoustic waves in polycrystalline diamond plates," Diamond Relat. Mater. 10, pp. 686-692, 2001.

[6] X. Jiang, J. Philip, W.J. Zhang, P. Hess, and S. Matsumoto, "Hardness and Young's modulus of high-quality cubic boron nitride films grown by chemical vapor deposition," J. Appl. Phys. 93, pp. 1515-1519, 2003.

[7] G. Lehmann, P. Hess, S. Weissmantel, G. Reisse, P. Scheible, and A. Lunk, "Young's modulus and density of nanocrystalline cubic boron nitride films determined by dispersion of surface acoustic waves," Appl. Phys. A 74, pp. 41-45, 2002.

[8] P. Mark, D'Evelyn, and T. Taniguchi, "Elastic properties of translucent polycrystalline cubic boron nitride as characterized by the dynamic resonance method," Diamond Relat. Mater. 8, pp. 1522-1526, 1999.

[9] P. Hess, "Determination of mechanical properties of superhard amorphous, nanocrystalline, and microcrystalline materials by laser-based surface acoustic waves" in: *Nondestructive Evaluation and Reliability of Micro- and Nanomaterial Systems*, N. Meyendorf, G.Y. Baaklini, and B. Michel, Editors, Proceedings of SPIE, Vol. 4703, pp. 1-13, 2002.

[10] J. Haines, J.M. Léger, and G. Bocquillon, "Synthesis and Design of Superhard Materials" Annu. Rev. Mater. Res. 31, pp. 1-23, 2001.