Elastic, mechanical, and thermal properties of nanocrystalline diamond films

J. Philip and P. Hess
Institute of Physical Chemistry, University of Heidelberg, D-69120 Heidelberg, Germany

T. Feygelson
GeoCenters Inc., Fort Washington, Maryland 20639

J. E. Butler
Code 6174, Naval Research Laboratory, Washington, DC 20375

S. Chattopadhyay, K. H. Chen, and L. C. Chen
Center for Condensed Matter Sciences, National Taiwan University, Taipei, Taiwan 106, Republic of China

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Nanocrystalline columnar-structured diamond films with 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} \, \text{cm}^{-2} were accomplished prior to growth by seeding with explosively formed nanodiamonds, which resulted in good optical quality films. The film thickness was measured in situ by the laser reflectometry method. The grain size and optical quality of the films were characterized by scanning electron microscopy and Raman measurements. Broadband surface acoustic wave pulses were used to measure the anomalous dispersion in the layered systems. The experimental dispersion curves were fitted by theory, assuming the diamond film as an isotropic layer on an anisotropic silicon substrate, to determine mean values of the density and Young’s modulus of the diamond films. The density was close to the density of single crystal diamond or polycrystalline diamond plates grown by the CVD technique, whereas the Young’s modulus varied strongly with the nucleation density between 517 and 1120 GPa. Young’s moduli close to the single crystal values were obtained for films grown with a nucleation density close to the single crystal values were obtained for films grown with a nucleation density >10^{12} \, \text{cm}^{-2}. The thermal diffusivity in these films was measured by the traveling wave technique. The value for ~3.5-μm-thick nanocrystalline diamond films with nucleation densities >10^{12} \, \text{cm}^{-2} was ~7.2 \, \text{cm}^2/\text{s}, whereas those with lower nucleation densities showed a value of ~5.5 \, \text{cm}^2/\text{s}. © 2003 American Institute of Physics. [DOI: 10.1063/1.1537465]

I. INTRODUCTION

Diamond is the material of choice for many scientific and technological applications because of its exceptional mechanical, electrical, thermal, and optical properties. In particular, the high hardness and stiffness of diamond make it desirable for many mechanical applications. For this reason there is great interest in the preparation of thin diamond films, which can be used as hard and wear-resistant coatings in a variety of applications, the preparation of diamond cantilevers for scanning force microscopy, or fabrication of high-Q and high-frequency micromechanical resonators. The extreme thermal conductivity in diamond has also propelled the material for heat spreader applications. While microcrystalline diamond films with thickness in the range of several micrometers have been successfully prepared and characterized, the interest in synthesizing diamond films with grain sizes in the nanometer scale (\sim 100 \, \text{nm}) is increasing. One reason is to reduce the intrinsic roughness of the diamond surface. However, such nanophase materials have grain size dependent mechanical properties that may significantly differ from those of their coarser–grained counterparts.

The changes in the mechanical properties due to reduction in grain sizes are due to the fact that a larger percentage of the atoms are expected to be in grain boundary environments with broken bonds, hydrogen termination, amorphous regions, and/or \( \text{sp}^2 \) bonded carbon. In addition, the mechanical properties will be affected by other features such as flaws, strains, impurities, etc., that result from synthesis and processing. Similarly the phonon scattering processes in diamond that determine its thermal conductivity are also dependent on the local bonding environment in the crystal as well as in the grain boundaries. Most of the defects and bonding nature, \( \text{sp}^2 \) or \( \text{sp}^3 \), that could affect the mechanical properties would affect the lattice thermal conductivity also. Therefore, it is very important to understand the mechanical and elastic properties before designing and fabricating complex mechanical structures. At present only limited information is available in the literature on the elastic properties, density, and thermal conductivity/diffusivity of nanocrystalline films. In the case of nanocrystalline cubic boron nitride films it has been found recently that the elastic properties may differ substantially from those of single-crystal \( c\text{-BN} \).
though the elastic and thermal properties of microcrystalline diamond films with a thickness in the range of a few micrometers have been investigated by the surfaces acoustic wave (SAW) method, and the traveling wave technique (TWT), respectively, no such work has been reported on nanocrystalline diamond films.

The “nanocrystalline” diamond films studied here are similar in their column structure to the thicker micro- or polycrystalline diamond films and plates studied previously, but very different from the “ultrananocrystalline” diamond films reported by Gruen et al. The present nanocrystalline films are grown on substrates coated with explosively prepared diamond, which promotes nucleation densities from $10^{10}$ to greater than $10^{12}$ nuclei/cm$^2$. Subsequent growth to a thickness of 100–5000 nm results in grain coarsening, polycrystalline texture development, and columnar growth yielding an anisotropic material whose local grain size depends on the distance from the nucleation layer and the growth conditions. The ultrananocrystalline films, on the other hand, have much less grain coarsening, significantly higher sp$^2$ carbon fraction (in fact the evidence for crystalline carbon is barely detectable with conventional techniques) and much higher optical absorption than the columnar nanocrystalline diamond films reported here.

The current techniques used to investigate elastic properties of thin film samples are Brillouin scattering, ultrasonic interferometry, nanoindentation, and the SAW method. Of these, the dispersion of SAWs is a very suitable technique to measure the elastic properties of superhard films. Thermal conductivity/diffusivity measurements in micro- or polycrystalline diamond were in general carried out by photothermal techniques which in some cases can probe within a grain. The TWT measurements could distinguish between the thermal diffusivity in the growth and nucleation zones of free-standing polycrystalline diamond plates and correlate it to the full width at half maxima of the 1332 cm$^{-1}$ line in the Raman spectra.

Raman and photoluminescence spectra were recorded to evaluate the phase purity of the films and scanning electron microscopy (SEM) to gain insight into the structure and morphology. These measurements indicate that the column diameters were in range of 10–100 nm.

II. EXPERIMENT

A. Sample preparation

The nanocrystalline diamond films studied in this work were fabricated by establishing a nucleation layer on 3 in. diameter, 3-mm-thick silicon substrates by: (1) first pre-treating the substrate to the diamond growth plasma conditions for a brief period of time (800 W microwave power, 720 °C substrate temperature, 900 sccm hydrogen flow rate, and 4 sccm methane flow rate), typically 10–30 min; then (2), putting the treated substrate into an ultrasonic bath of nanocrystalline diamond powder in methanol or ethanol for 10–60 min; followed by (3), immediate rinsing and washing with ethanol and nitrogen blow dry. This is an implementation of the nucleation process reported by Rotter. For film growth, the seeded substrate is returned to the growth reactor and diamond is grown to the desired thickness at the conditions given earlier. The growth rate and film thickness were monitored in situ by diode laser reflectometry at 677 nm. Uniform and conformal nucleation densities in excess of $10^{12}$ cm$^{-2}$ were observed on Si and SiO$_2$. The growth reactor was a commercial microwave plasma reactor (model PDS-17, Astex Inc., Woburn, MA) operating at 2.45 GHz with a maximum power of 1.5 kW.

Purified hydrogen and methane (99.999%) were used as reactants. The substrate was placed on an inductively heated susceptor and the pressure of the flowing gases was maintained at 15 Torr. This reactor had been used previously for growth of boron doped diamond films using diborane as a reactant. Analysis of films similar to the ones studied in this work has indicated residual boron doping levels of $10^{19}$–$10^{20}$ boron atoms per cubic centimeter.

B. Raman and SEM measurements

Micro-Raman and photoluminescence spectra were measured using Ar-ion laser excitation at 488 nm and a commercial confocal micro-Raman spectrometer (Renishaw $\times 1000$) using a 50× microscope objective. The approximate laser spot size on the sample was 1 μm in diameter and the laser power was less than 2 mW.

Scanning electron micrographs were obtained in a commercial field emission SEM (Leo-1550) with no coatings applied to the samples. The nucleation surface was prepared for SEM examination by etching the silicon substrate with a combination of hydrofluoric, acetic, and nitric acids.

C. Surface acoustic wave dispersion measurements

In this technique the surface of the sample is irradiated with nanosecond laser pulses to generate broadband SAW pulses. These pulses propagate over a known distance and are detected with a suitable broadband transducer. The presence of the film on the substrate surface introduces a length scale, and thus generates the dispersion effect, which contains the information on the elastic and mechanical properties of the film and substrate system. If the substrate properties are known, one or more film properties can be extracted from a theoretical fit of the nonlinear dispersion curve.

We report here on measurements performed on three separate nanodiamond films with varying thickness (see Table I). Samples D1 and D2 were the initial batch prepared. Sample D5 was prepared several months later after a problem with the solution used to seed the nucleation layer was discovered and corrected. All films were deposited on 3 in. diameter Si(100) substrates with 3 mm thickness. The thickness of the films varied between 0.6 and 4.1 μm and was determined by in situ laser interferometry at 677 nm during growth near the center of the film, and at other points displaced from the center, by counting the number of interference fringes (Newton’s rings) under 546 nm light. These measurements were confirmed by Fourier-transform infrared (FTIR) transmission and reflection measurements using the refractive indexes: $n_{VIS}=2.41$ and $n_{IR}=2.378$ and SAW measurements performed at different locations of the wafers to realize different film thicknesses. In order to ensure that
the film thickness did not vary significantly over the propagation distance of the SAW pulse, the direction of SAW propagation was selected to be parallel to the (110) direction of silicon and tangential to the circular interference fringes. Since the Rayleigh wave velocity in diamond is significantly higher than in silicon, the phase velocity strongly increases with frequency in the layered system (anomalous dispersion). Frequency components up to about 250 MHz could be detected. A good signal-to-noise ratio was achieved up to 100 MHz for the thicker films and up to 170 MHz for the thinner films. The same experimental conditions were maintained for the measurements performed at different thickness values.

D. TWT for the determination of thermal diffusivity

The diamond films on silicon were systematically studied for the thermal diffusivity by the TWT. The method of determining the thermal diffusivity from the phase lag between a temperature forcing function and the traveling thermal wave in the material was described by Kosky.\textsuperscript{18} The present technique uses a probe laser to compare the phase instead of a IR microscope to determine the actual temperature in the material. A sine wave (2 Hz) modulated GaAs (SDL-3490-S) diode laser (\(\lambda = 812\) nm) was used to generate a sinusoidal thermal wave in the thin film by irradiating the edge of the sample with the laser. By monitoring the phase difference (\(\Delta \theta\)), from the deflection of a He–Ne probe laser beam (15 mW, Melles Griot), as a function of the distance (\(d\)) along the sample, the thermal diffusivity (\(\alpha\)) is determined. The relation between the phase difference (\(\Delta \theta\)) at a particular point on the sample as detected by the probe laser and the distance (\(d\)) of that point from the IR source is given by

\[
\Delta \theta = \frac{\pi}{4} + \left( \frac{180}{\pi} \right) \sqrt{\frac{f}{\alpha \cdot d}}.
\]

where \(f = 2\) Hz is the frequency of the modulating sine wave. The slope of the \(\Delta \theta\) vs \(d\) plot yields the value of the thermal diffusivity. The details of the thermal diffusivity measurement setup are given elsewhere.\textsuperscript{19}

Graebner et al.\textsuperscript{12} reported anisotropy in the thermal conductivity of chemical vapor deposition (CVD) diamond measured by a laser flash technique and fast infrared detection. Ono et al.\textsuperscript{20} reported the thermal conductivity values of microwave CVD diamond films by making use of radiation heat transfer and radiation thermometry. Irrespective of the method used, the measurement and the interpretation of the results become complicated for a thin film on a particular substrate, as in this case, where the heat is conducted both by the film and the substrate.

III. RESULTS

Table I presents a summary of the growth conditions, the film thicknesses, the results of the SAW dispersion analysis, and thermal diffusivity measurements for the diamond films investigated. Photographs of the films D1 and D2 are shown in Figs. 1(a) and 1(b), respectively, where the samples are illuminated with monochromatic light (546.1 nm). Interference fringes, Newton’s rings, are observed as a result of the variation in film thickness with position on the wafer. A scanning electron micrograph (SEM) of a portion of the growth surface of films D2 and D5 are shown in Figs. 2(a) and 2(b), respectively, while SEMs of portions of the initial nucleation surfaces of the films D2 and D5 are shown in Figs. 3(a) and 3(b), respectively. Figure 4(a) presents the micro-Raman spectra and Fig. 4(b) presents the photoluminescence spectra of samples D2 and D5, excited by 488 nm Ar-ion laser radiation, including the Raman scattering portion of the spectra. Figures 5(a) and 5(b) display the micro-Raman spectra recorded at different distances from the center of the wafer (thickness values) for the films D2 and D5.

Figure 6 shows two SAW pulses measured for a 2-\(\mu\)m-thick nanodiamond film. Pulses (a) and (b) in the figure were detected at distances of 6.2 and 14.2 mm from the excitation line, respectively. Figure 7 presents the dispersion curve resulting from the Fourier transformation of these two SAW pulses. As can be seen, the phase velocity increases with frequency, as expected for the stiffer diamond film (anomalous dispersion). Due to the large acoustic contrast between the silicon substrate and the diamond film the dispersion curve is strongly nonlinear. The best theoretical fit to the experimental dispersion curve is also shown in Fig. 7, and was used to extract the values of the Young’s modulus, thickness, and film density.

The value of the Poisson’s ratio was fixed to 0.12 ± 0.04, the value reported in the literature for microcrystalline diamond. It should be noted that the values of the Young’s

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Growth conditions</th>
<th>Laser interferometry</th>
<th>Reflection FTIR ((\mu m))</th>
<th>SAW measurements</th>
<th>TWT measurements</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Est. error)</td>
<td>Time (min)</td>
<td>% CH(_4) in H(_2)</td>
<td>during growth ((\mu m))</td>
<td>Reflection ((\mu m))</td>
<td>(\rho) (g/cm(^3))</td>
</tr>
<tr>
<td>D1</td>
<td>905</td>
<td>0.33</td>
<td>1.61</td>
<td>1.41</td>
<td>(±0.2)</td>
</tr>
<tr>
<td>D2</td>
<td>905</td>
<td>0.88</td>
<td>3.45</td>
<td>2.98</td>
<td>2.0</td>
</tr>
<tr>
<td>D5</td>
<td>1605</td>
<td>0.33</td>
<td>3.61</td>
<td>3.6</td>
<td>3.4</td>
</tr>
<tr>
<td>CVD plate</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3.6</td>
</tr>
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</table>

Growth conditions and Laser interferometry are given elsewhere. SAW measurements were used to extract the values of the Young’s modulus, thickness, and film density.
modulus and density determined by the SAW method do not depend sensitively on the Poisson’s ratio. For example, a variation in the Poisson’s ratio by 33% changes the Young’s modulus and density only by a few percent.

The best theoretical fits of the experimental dispersion curves yielded densities in the range of \(3.47\pm0.15\) g/cm\(^3\), irrespective of the thickness of the film. This value is to be compared with 3.515 g/cm\(^3\) reported for single crystal diamond and indicates a surprisingly high density of all three films. The relatively large error in the density values seems to be mainly due to a coupling of the Young’s modulus and density in the SAW analysis applied.

The values of the Young’s moduli obtained in the thickest region of the D1 and D2 films were in the range of \(517\pm30\) GPa, whereas for the film D5 we measured a value of \(1120\pm30\) GPa. A plot showing the variation of the Young’s modulus with film thickness is presented in Fig. 8. The stiffness slightly decreases in the direction of decreasing film thickness at the edge of the wafers but this effect is in the range of the experimental error. The measured moduli should be compared with 1080\,\pm\,20 GPa reported previously for a micrometer thick microcrystalline diamond film and 1143 GPa estimated theoretically for ideal polycrystalline diamond, where it is assumed that the grain boundaries do not influence the elastic properties.

Note the substantial difference between the results for the first batch of samples D1 and D2 and sample D5. The first two samples were grown using a nucleation solution of nanodiamonds, step 2 in the nucleation procedure described earlier, which had gradually become depleted of seeds, resulting in incomplete coverage and lower nucleation density with regions of amorphous carbon between nuclei, as can be seen in Fig. 3(a). A comparison of Figs. 3(a) and 3(b) shows a remarkable difference in the nucleation densities, \(~10^{10}\) nuclei/cm\(^2\) for film D2 [Fig. 3(a)], versus over \(5\times10^{11}\) to greater than \(10^{12}\) for film D5 [Fig. 3(b)]. SEM images of the nucleation layer for film D1 are consistent with that shown for film D2, while the SEM for film D5 is consistent with other samples grown from a more concentrated solution of seeds. Attempts at optimizing and quantifying the particle size distribution and concentration in the solution are in progress.

In order to compare the Young’s modulus of the nanocrystalline diamond films with that of a thicker polycrystalline diamond plate, a plate of thickness 400 \(\mu\)m was grown by CVD on a polished tungsten plate in a similar 5 kW microwave plasma reactor. The plate was polished down to a thickness of 320 \(\mu\)m. The Rayleigh velocity of surface acoustic waves on the plate was measured by laser excitation of SAWs and detection after propagation over a known distance with the piezoelectric foil detector. The longitudinal...
acoustic bulk wave velocity in the plate was determined by a transmission technique, employing laser excitation on one and detection on the opposite side of the plate. Assuming the polycrystalline plate as isotropic, the mean value of the Young’s modulus was evaluated following well-known equations. The experimental results could be described with a density of the plate of 3.52 g/cm$^3$, a Rayleigh velocity of 10750$^{\pm}$680 m/s, a longitudinal acoustic bulk velocity of 17980$^{\pm}$100 m/s, a Poisson’s ratio of 0.089$^{\pm}$0.03, and a Young’s modulus of 1120$^{\pm}$30 GPa. This indicates that the mean stiffness of this thick plate was comparable to that of sample D5 demonstrating the high quality of this diamond sample.

Thermal diffusivity measured on samples D1, D2, and D5 are tabulated in Table I. A considerable thickness effect on the thermal diffusivity was observed for these films. Sample D5 was found to have substantially higher (>25%) thermal diffusivity value than sample D2, which is of a similar thickness as sample D5. Assuming the density and specific heat values of single crystal diamond for the nanocrystalline samples, the thermal conductivity of these nanocrystalline diamond samples could be arrived at, which are also shown in Table I. Thermal conductivity values were in the range of 5–14 W/cm K, whereas for natural diamonds this value can go up to 25 W/cm K. Figure 9 shows a comparison of the thickness dependence of the thermal diffusivity in sample D5, prepared under high nucleation densities, and another sample prepared under low nucleation densities.

Both samples show a strong thickness dependence, which was not as pronounced in the SAW measurements, but clearly sample D5 was the superior one having a higher range of thermal diffusivities.

### IV. DISCUSSION

Usually the Young’s modulus or stiffness of a film correlates with its density. As is evident from the values presented in Table I, the Young’s modulus of the nanodiamond films D1 and D2 is only about half the value found for the high quality nanodiamond film D5 and the plate. On the other hand, the corresponding density values vary only by a few percent. Since the experimental error in the density is in the same range as the differences measured for the three film samples and the plate, it is not possible to extract from these density values more detailed information on the reason for the strong reduction of the stiffness in films D1 and D2.

The micro-Raman and photoluminescence spectra of the films exhibit a broadened diamond zone center phonon mode at 1332 cm$^{-1}$, Raman scattering between 1340 and 1600 cm$^{-1}$ associated with resonance enhanced Raman scattering from $sp^2$-bonded carbon, and a broad background photolu-
minescence from 500 to 800 nm. The broad photoluminescence is likely due to the presence of electronic states in the band gap of diamond due to dislocations and extended defects within the grains. There is no evidence of photoluminescence from nitrogen vacancy centers with zero phonon lines at 575 and 637 nm, which are frequently seen in CVD diamond materials. The weak broad luminescence at 737 nm is likely due to a trace of the Si–V center, also frequently seen in CVD diamond.

The high density of these films, coupled with the faceted grain structure observed in the SEM, and low $sp^2$-bonded carbon content, is consistent with a material comprised of bulk crystalline diamond domains separated by incoherent grain boundaries, probably containing many twin related grains, stacking faults, and stress induced dislocations. Transmission electron microscopy studies of thicker polycrystalline CVD diamond films have demonstrated this general structure beginning with growth of individual nuclei until they coalesce into a film, followed by rapid overgrowth of most nuclei by a few preferentially oriented nuclei (or growth sectors). Then further grain coarsening or enlarge-
leads to more rapid film coalescence and thus less volume of particular sample. A higher nucleation density during growth responsible for the systematically lower Young’s moduli constants increases with decreasing film thickness and may be on the mean values of the elastic and mechanical con-

films. The SEM pictures indicate nucleation transition layers during growth on the elastic properties of nanodiamond grains separated by fewer grain boundaries with a columnar structure, it is not possible to identify the weak bonding effects from the measured mean values of the mechanical properties. We are led to conclude that the presence of weaker three-dimensional bonding, e.g., by amorphous or sp²-bonded carbon at the grain boundaries, which does not have long-range order, causes the substantial reduction in the Young’s modulus without significantly reducing the density.

Intergrain and intragrain phonon scattering are believed to be the dominant factors in determining the mean thermal diffusivity characteristic of the particular sample. Intergrain scattering is mostly dominated by the sp²-rich grain boundaries, whereas defects within a crystal dominate the intragrain scattering. For reasons mentioned earlier for the elastic properties, here also sample D5 has a 25% higher thermal diffusivity than sample D2 probably due to less intergrain scattering. However, this was much less than the observed difference in their Young’s modulus (~100%). Physical properties, such as density, that were found to have a considerable effect on the thermal diffusivity of a material, were similar for these nanocrystalline diamonds. This may be one of the reasons for not observing a drastic change in thermal diffusivity in these samples. Generally one would have expected a change in mass density of the films when the grain density is changing. Hence, in this case the change in the thermal diffusivities in D2 and D5 should relate more to the crystalline quality of the samples. The thickness dependence of thermal diffusivity shown in Fig. 9 should be largely due to the anisotropy across the thickness of the sample. The quality of the grains and the defective grain boundaries are all complex functions of growth time. Moreover, the interface between the film and the substrate will also produce some interfacial thermal resistances that will change with growth time and, hence, thickness of the film. The improving quality of crystals and reducing interfacial thermal resistance with the thickness of the film will translate into an increasing thermal diffusivity. A detailed description of this thickness dependence of thermal diffusivity in thin film on substrate systems is given elsewhere. Interestingly, the thermal diffusivity/conductivity values reported for polycrystalline CVD diamond films are close to the values found for these nanocrystalline diamonds.

V. CONCLUSION

The mean values of the Young’s modulus and density of three nanocrystalline diamond films and a free-standing diamond plate were determined by analyzing the measured dispersion of broadband laser-generated SAW pulses. The thermal diffusivity of these nanocrystalline diamond materials grown under high and low nucleation density conditions was measured by the traveling wave technique. The morphology of the films was determined by SEM and bonding information was extracted by micro-Raman. It was found that the Young’s moduli of the nanocrystalline films grown with lower nucleation densities (10¹⁰ cm⁻² or lower) was roughly half of those of a film and plate grown with much higher nucleation density (≥10¹² cm⁻²). For diamond grown with high nucleation density, the Young’s modulus was close to

![Graph: Variation of thermal diffusivity with the thickness of nanodiamond samples grown under nucleation densities (■)≈10¹⁰ cm⁻² (sample D5) and (□)≈10¹² cm⁻².](image-url)
the corresponding values measured for high quality microcrystalline films or a polycrystalline diamond plates grown by the CVD technique. On the other hand, the density of the films was rather independent of the nucleation density and agreed within a few percent with the value of single crystal diamond. The thermal diffusivity value for the nanocrystalline film grown under high nucleation densities was found to be 25% higher than of films grown under low nucleation densities. A strong thickness dependence of the thermal diffusivity was observed in these nanocrystalline diamond films that could be due to the crystalline quality and volume fraction, and interfacial thermal resistance in the layered structure, all of which are functions of growth time.

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14 R. Kalish, C. Saguy, and J. E. Butler (private communication).