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Optical properties of nanocrystalline diamond films by prism coupling technique

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Measurement of optical properties such as the refractive index and thickness of nanocrystalline or smooth diamond films is carried out by the prism coupling technique. The films observed to be absorbing for a standard operating wavelength of 633 nm and higher wavelengths, i.e., 830 and 1300 nm, were used to obtain sharp guided modes and the refractive index and thickness of the films could be measured independently with high accuracy. The index of the nanocrystalline diamond films was found to be homogeneous within the films with negligible changes observed at the film–substrate interface. Information on absorption was also obtained from the half width of the guided modes and was correlated to the graphitic concentration of the films measured by Raman spectroscopy. The thickness measured by the prism coupling technique was found to be in agreement with the thickness measured by cross-sectional transmission electron microscopy. The overall results indicate that the prism coupling technique can be very useful for rapid, easy accurate measurement of the refractive index and thickness of smooth diamond films. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1524719]

I. INTRODUCTION

The prism coupling technique[1–3] is a proven technique to rapidly and accurately measure both the thickness and refractive index of dielectric and polymer films[4] and is also used widely as a powerful technique to measure the optical constants of AlGaN films[5,6] and other films.[7–10] It has unique advantages over other conventional techniques such as ellipsometry, spectrophotometery, etc. to measure these thin film parameters since no advance knowledge of the film thickness or index is required, so measurements of these parameters can be done easily and rapidly (20 s) with extremely low standard deviation (typically 0.3% for the thickness and 0.1% for the index). Although this technique is used to characterize many kinds of thin films,[4–10] diamond and related thin films have not been measured in detail before. The high surface roughness of conventional diamond film, which is called microcrystalline diamond (MCD), with the crystal size of the order of a few micrometers, is a major problem in characterizing them using this technique. Recently, we have succeeded in growing very smooth nanocrystalline diamond (NCD) films on Si substrates by a processing method called biased enhanced growth (BEG) in microwave plasma chemical vapor deposition (MPCVD).[11,12] This method, which can be considered an extension of biased enhanced nucleation[13] of diamond, offers nucleation and growth in a single process unlike the conventional two or three stage processes for heteroepitaxial growth of diamond.[14–16] The BEG process is also different from the process that uses carbon dimers (C_2) as the growth species in hydrogen deficient plasmas (CH_4/Ar or C_{60}/Ar) for growth of NCD films.[17] The NCD film is a layer composed of a high concentration of diamond crystals a few to several tens of nanometers in size with a significant amount of nondiamond carbon decorating the grain boundaries. Here we show use of the prism coupling technique to measure optical properties such as the refractive index and thickness of smooth NCD films on silicon substrates and discuss the optical losses in such films as well as correlating them to their structural properties.

II. EXPERIMENT

The NCD films were grown in a 2.45 GHz Seki Technotron Corporation, Tokyo, Japan (formerly Applied Science and Technology, USA) made MPCVD system on mirror polished Si(100) substrates using BEG, an extension of biased enhanced nucleation[13] recently developed by our group.[11,12] In brief, controlled continuous bias current density (BCD) was provided to the substrates with 5% methane balanced with hydrogen at 1000 W microwave power and 30 Torr pressure. A quartz shield was used to cover the conducting parts of the substrate holder assembly (other than the substrate), while applying negative bias to the substrate throughout growth to enhance the BCD in the substrate at low microwave powers without affecting the microwave plasma. The substrate temperature, which was measured at the bottom of the graphite substrate holder by a thermocouple, was kept constant at 600 °C. Four films were grown at the same conditions for 60, 90, 120 and 240 min. The refractive index and thickness of the films were measured by a Metricon model 2010, Pennington, New Jersey, USA, based on the

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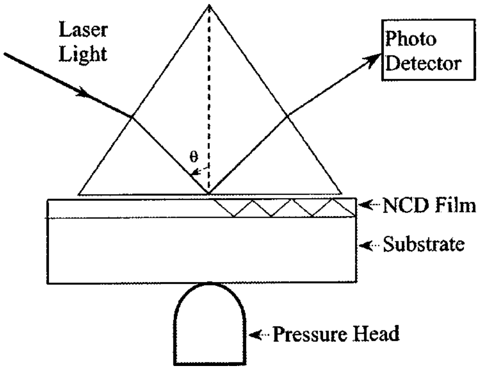

FIG. 1. Schematic of the prism coupler.

prism coupling technique. Transmittance and reflectance measurements were carried out in the wavelength range of 200–2000 nm after opening a small window on the backside of the substrate by chemically etching. Cross-sectional transmission electron microscopy (TEM) was used to examine the thickness of the samples. The surface roughness was measured using atomic force microscopy (AFM) and other structural characterizations were carried out by micro-Raman spectroscopy (STR250, Seki Technotron Corporation, Tokyo, Japan) at 514.5 nm.

Structural characteristics of the films show that the films consist of NCD and have been discussed in detail elsewhere.[12,18,19] The prism coupling technique has been described in the literature in detail.[1–5] In brief, the film thickness and optical constants can be determined together at any point on the sample by observing the wave guiding modes of the sample. The film surface is attached to the base of a right-angle prism by means of a pneumatically operated coupling head, shown in Fig. 1. This arrangement for holding the sample leaves a small gap of air between the film and the prism. A laser beam is sent to the base of the prism and reflection is measured by a photodetector. The guided spectrum of the sample is plotted by measuring the reflected intensity with respect to the angle of incidence of the beam. Dips in the intensity are observed at certain discrete values of the incident angle of the laser beam. At these particular incident angles, light tunnels through the air gap into the film and enters into guided optical propagation modes, resulting in a drop in reflected intensity of the light. The angular location of the modes determines the film index, whereas the difference in angular locations determines the thickness.

III. RESULTS AND DISCUSSION

Figure 2 illustrates the guided spectra of the films, grown for 60, 90, 120 and 240 min. at the same conditions. The vertical lines in Fig. 2 exhibit the guided modes observed in the spectra of different films. Operating wavelengths of 830 and 1300 nm were used for all the measurements. The reason for not using the standard wavelength (633 nm) lies in the fact that our NCD films are absorbing for shorter wavelengths,[19] as can be seen in Fig. 3 in the transmittance spectrum of the film grown for 60 min. High absorption may lead to higher standard deviation of the measurements. It was also observed that the intensities of the dips at 830 nm decrease with film thickness, obviously because of an increase in the optical path length of the guided light in the films. Figure 2 shows the guided spectra of films deposited for 90 min taken at both wavelengths. Although the number of modes increases by decreasing the wavelength, as expected, the intensities of the dips decrease significantly, making it difficult to accurately identify their locations. Therefore, guided modes in the films grown for 60 min could be measured with good accuracy using 830 nm only whereas guided modes in the films grown for 120 and 240 min could be measured using 1300 nm. Since the films grown for 90 min lie between the two conditions (thickness and absorption of the wavelength at 830 nm), guided modes are observed for both wavelengths. However, it should be mentioned that the guided modes of the MCD films, which have low absorption throughout these regions (Fig. 3), can be measured accurately even at lower wavelengths provided that their surfaces are smooth enough not to have high surface scattering losses.

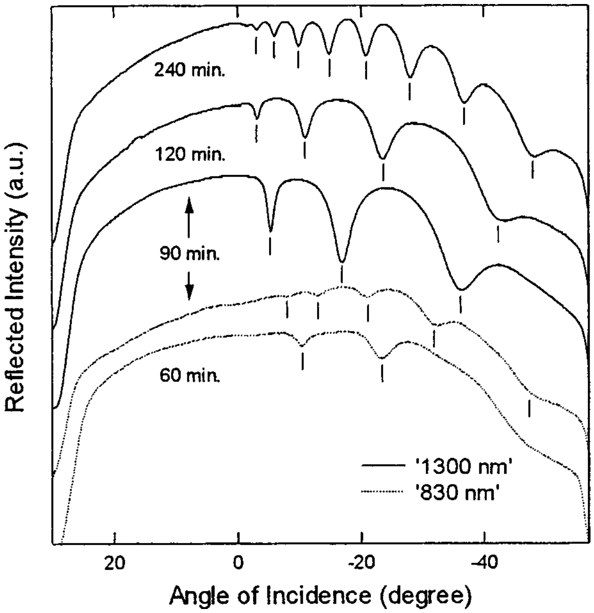

FIG. 2. Guided mode spectra of NCD films grown for various deposition times (60, 90, 120, and 240 min) at 830 and 1300 nm. The vertical lines represent the guided modes in the films.

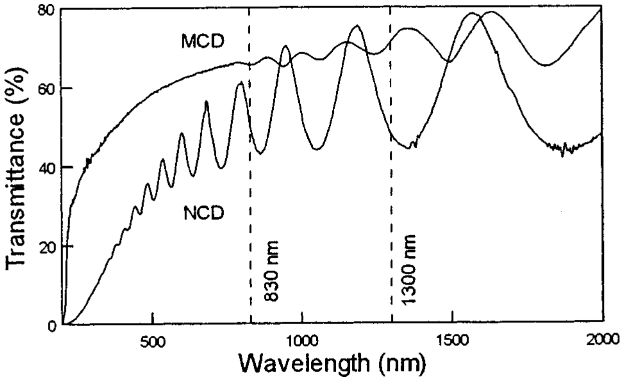

FIG. 3. Transmittance spectra of a MCD film and the NCD film grown for 60 min.

TABLE I. Refractive index and thickness of the films at different wavelengths.

Deposition time (min) ⇓ At wavelength ⇒	Refractive index		Thickness		Roughness
	(±0.001)		(±0.5%+0.005) μm		±2.00 nm
	830 nm	1300 nm	830 nm	1300 nm	
60	2.3478	⋯	0.8833	⋯	20.13
90	2.3456	2.3306	1.4847	1.4992	24.50
120	⋯	2.3373		1.8636	33.10
240	⋯	2.3349		4.1008	26.83

The refractive index and thickness of the films calculated are summarized in Table I. The refractive index of the films grown for 60 and 90 min at 830 nm is exactly the same within measurement error. Also, the refractive indices of 90, 120 and 240 min films are the same up to the second decimal point at 1300 nm. However, the values of the index at higher wavelength are lower which is expected. In general the indices of the NCD films are a little low compared to the index of MCD or natural diamond (2.41 at 633 nm),[20] but are in agreement with the index of fine grain diamond films measured by the same technique.[21] The refractive index of the film grown for 60 min was also measured by a reflectance spectrum of the same film using the basic equation for interference fringes.[22] The thickness was taken from the cross-sectional TEM that is described in the following. The index value was found to be 2.3111±0.0500 at 790 nm, which matches (within measurement error) well the value obtained by the prism coupling method at 830 nm (Table I).

Figure 4 shows the index profile of the samples grown for 120 min reconstructed from the effective indices at 1300 nm using Chiang's algorithm.[23] The index is maximum at the surface and remains fairly constant throughout the thickness and decreases rapidly near the film/substrate interface. This index characteristic indicates uniformity of the index with depth with a perfect step change in index at the interface.[6,24] It in turn shows the uniformity of the film with thickness that perfectly matches the result of the constant value of the index of different films grown for different thicknesses. It also indicates that the interfacial layer is negligibly thin so as to not have any effect on the index characteristics of the film. The constant index of the films with different thicknesses and the homogeneous index within the films indicate the consistency and reproducibility of the BEG process to grow NCD films in a MPCVD system.[11,12]

The calculated thickness of the samples (Table I) varies linearly with the deposition time as expected. To further examine the validity of the prism coupling technique to measure the thickness of NCD films, the NCD film grown for 60 min was subjected to cross-sectional TEM analysis. Figure 5

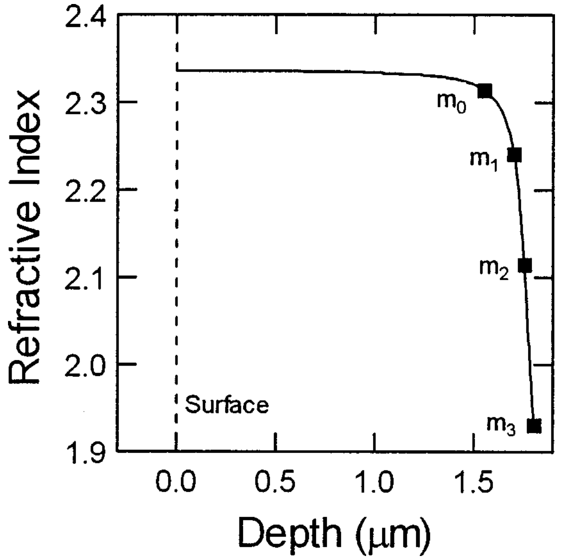

FIG. 4. Refractive index profile of the films grown for 120 min reconstructed from measurements at 1300 nm. Points m_0–m_3 are the points shown by vertical lines in the guided spectrum of the same film in Fig. 2.

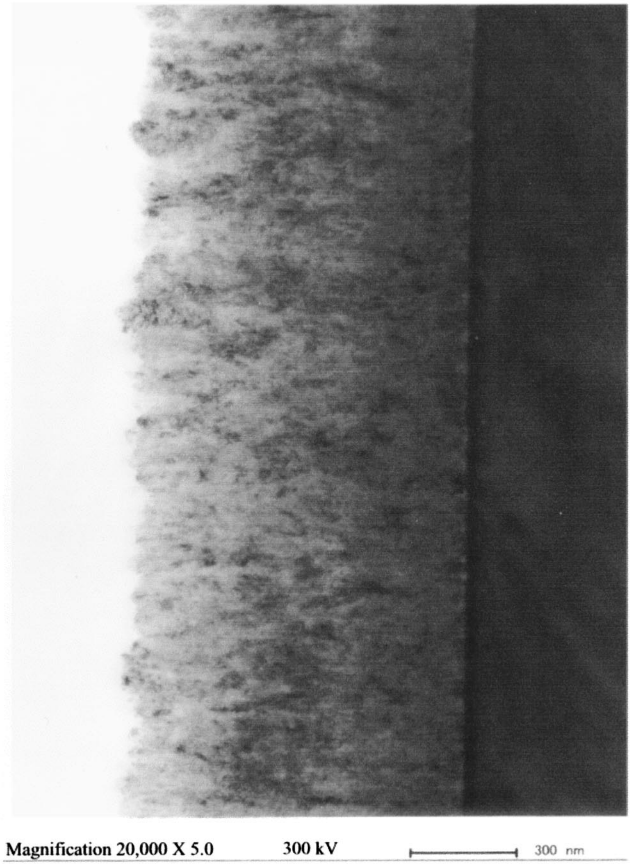

FIG. 5. Cross-sectional transmission electron microscopy micrograph of the films grown for 60 min. The thickness of the film is approximately 940 ±20 nm. The error in measurement comes mostly from the surface roughness of the film.

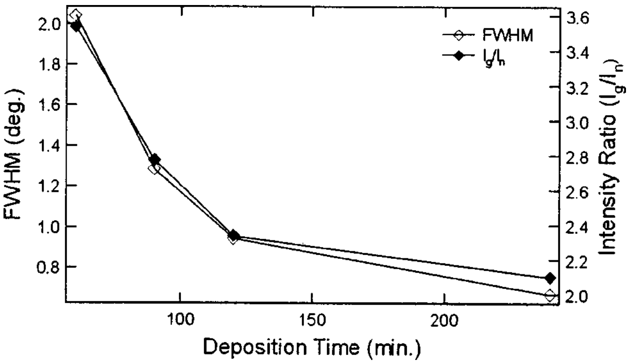

FIG. 6. Plots of the half width and the Raman intensity ratio of the *G* band to the NCD band, I_g/I_n, as a function of the deposition time.

shows the cross-sectional TEM micrograph. The thickness measured is approximately 940±20 nm, which is in agreement with the thickness measured by the prism coupling technique (883±10 nm). However, a little lower value of the thickness, as measured by prism-coupling technique, would have been a result of some absorption at the operating wavelength of 830 nm (Fig. 2). This means that the value measured using higher wavelength in other samples will have much less error. This demonstrates the usefulness of the prism coupling technique for accurate, reliable convenient measurement of film thickness, especially since no special sample preparation is needed in this nondestructive technique and that the measurements can be done in a very short time. In fact, this technique can be even more useful for MCD films, which are polished for optical and other applications. In those films the refractive index and thickness can be measured with high accuracy even at lower wavelengths because of their much lower absorption at those wavelengths (Fig. 3). Furthermore, the TEM image confirms the uniformity of the deposition of NCD, which matches to the results of the uniformity of the refractive index (Fig. 4).

Information on the absorption and surface roughness can also be assessed by the mode spectra, since the sharpness of the dips in the mode spectra should depend on optical losses of the incident beam.[25,26] The main loss mechanism could be scattering at surfaces and interfaces, and absorption within the film and at the film–substrate interface.[25,26] The half width of the first guided mode in the films (90–240 min at 1300 nm and 60 min at 830 nm) is plotted in Fig. 6. It is observed that the half width of the guided modes decreases with the deposition time. The root mean square (rms) surface roughness of the films, measured by AFM, is given in Table I. However, no correlation is observed in the surface roughness and half width and the film–substrate interface should be almost the same in the films because they are grown at the same conditions, suggesting absorption as a major factor that derives the half width of guided modes. The absorption of light in the NCD films should mainly arise from the graphitic content of the films. The relative concentration of the graphitic content of the films can be measured by Raman spectroscopy. Visible Raman spectra of the films grown for different deposition times are shown in Fig. 7. In brief, the visible Raman spectra of the films consist of a band near 1140 cm^{-1}, associated with the presence of diamond nanocrystals, along with features near 1350, 1470, and 1580 cm^{-1}. The band near 1470 cm^{-1} may be related to disordered sp^3 carbon in the films whereas the other bands near 1350 and 1580 cm^{-1}, respectively, are known to be graphitic *D* and *G* bands. In our films the relative intensity of the NCD band (I_n) to the graphitic *G* band (I_g) is found to have a correlation to structural and mechanical properties of the films and can be understood to represent the concentration of NCD in the films.[11,12,18,19] The relative concentration of the graphitic content derived from the Raman spectra of the films as a ratio of the *G* band to the NCD band (I_g/I_n) is plotted in Fig. 6. A good correlation between the half width and the graphitic content of the films is evident from the plots. This indicates that the absorption in the NCD film is associated with the presence of a graphitic component in the NCD films. Therefore, in general, the prism coupling technique can also be used to assess the quality of the NCD films in terms of optical losses that occur due to different mechanisms.

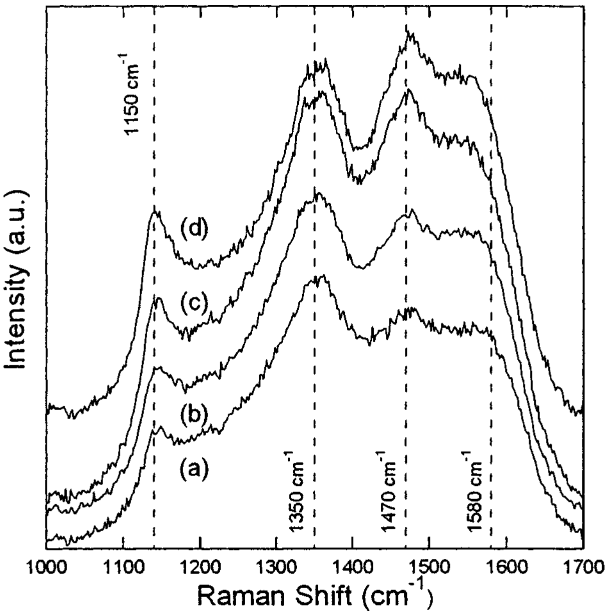

FIG. 7. Raman spectra of the NCD films grown for 60 (a), 90 (b), 120 (c) and 240 (d) min.

IV. CONCLUSION

It was shown that the refractive index and thickness of NCD films can be measured accurately by the prism coupling technique. The index of the NCD films was found to be homogeneous within the films with negligible changes observed at the film–substrate interface. Information on absorption was also obtained from the half width of the guided modes and was correlated to the graphitic concentration in the films measured by Raman spectroscopy. The overall results suggest the reliability and consistency of the continuous controlled bias current density process to grow NCD in a MPCVD system.

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