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Optical constants and thermo-optic coefficients of nanocrystalline diamond films at 30–500 °C

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The refractive index and absorption index of nanocrystalline diamond (NCD) films were investigated using spectroscopic ellipsometry between 30 and 500 °C. Due to their high transparency the experimental spectra could be well fitted in the subgap region using a single-oscillator model with a four-phase layered structure. The single-oscillator model yields a small optical absorption in the band gap region. The temperature dependence of dispersion of the refractive index over the photon energy range of 1.15–4.75 eV was determined. Based on the Bose-Einstein model, a thermo-optic coefficient of $(1/n)(\partial n/\partial T)=6.5\times10^{-6}$ K^{-1} at 300 K was obtained for the NCD film in the near-infrared region. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2243863]

Knowledge of the temperature dependence of optical constants (index of absorption and refractive index) of photonic materials is of fundamental importance in optoelectronics.[1,2] In particular, the thermo-optic effect is of relevance in many fields, such as optoelectronic switches, optical fibers, and laser techniques. Experimental data on the thermo-optic coefficient of the bulk semiconductors Si, GaAs, InP, SiC, and diamond have been published.[1–3] However, thin-film optical devices are especially attractive because of their potential for monolithic integration in high-speed electronic and optoelectronic systems. Among these materials high-quality diamond films may play an important role in high-temperature electronic devices due to their large band gap and thermal conductivity.[4,5]

The rough surfaces and high friction coefficients of microcrystalline diamond (MCD) films have initiated efforts to fabricate smooth nanocrystalline diamond (NCD) films.[6–10] While detailed experimental and theoretical studies on the optical properties of bulk diamond are available at different temperatures,[3,4,11–13] the more diverse structural properties and optical behavior of NCD films need further investigation. Better insight into the variety of nanostructures realized with different deposition techniques is of fundamental importance. No systematic studies of the optical constants have been performed which help to judge the quality of the material.[14] Spectroscopic ellipsometry (SE) is a unique and powerful tool to investigate the optical behavior of NCD films together with their thickness in a very wide photon energy range.[15,16]

Recently, high-quality NCD films with excellent elastic and mechanical properties, such as high Young's modulus, have been deposited.[10] These films are suitable as strong mechanical protective coatings with lower wear than MCD films. The wide optical band gap and low absorption in the near-infrared (NIR)-ultraviolet (UV) region are a critical issue in applications such as transparent coatings in optical components that may be used in a wide temperature range.

The NCD film used in the present investigation was grown on a *p*-type silicon (100) wafer by microwave plasma-enhanced chemical vapor deposition and structurally characterized as described previously (see sample B8 in Ref. 10). The lower limit of the grain size in the NCD film was estimated to be 10 nm embedded in a columnar-type structure.[10] Ellipsometric spectra were measured in the photon energy range of 1.15–4.75 eV at an incident angle of 76.7° ±0.1° by NIR-UV ellipsometry (ES4G OMA by Sopra, Inc.). The sample was fixed to a heatable holder in an ultrahigh-vacuum chamber ($<10^{-8}$ mbar). Altogether nine temperatures between 30 and 500 °C were studied that were measured by a thermocouple in good thermal contact with the sample, with an accuracy of ±2 °C of the set point.[17]

SE deals with the measurement of the relative changes in the amplitude and phase of the *s* and *p* components of linearly polarized light upon oblique reflection from the sample.[16] The experimental SE parameters, the angles Ψ and Δ, are defined by the relation $\rho=\tan\psi\exp(i\Delta)$, where ρ is the complex ratio of the two reflection coefficients. The dielectric response functions of the NCD films could be expressed by the following single-oscillator model:

$$\tilde{\varepsilon}(E)=(n+i\kappa)^2=\varepsilon_\infty+\frac{AE_0^2}{E_0^2-E^2-i\Gamma E}. \quad (1)$$

Here A, E_0, and Γ are model parameters and E is the photon energy. Note that the high-frequency dielectric constant ε_∞ was found to be unity. The dielectric functions of the silicon substrate were measured first at the corresponding temperatures and compared with literature data.[15] The four-phase model air/surface rough layer (SRL)/NCD/silicon was found to reproduce the ellipsometric spectra quite well, due to the well-defined NCD/Si interface.[10] The dielectric function of the SRL was expressed using the Brüggeman effective medium approximation (EMA). A small thickness inhomogeneity of ~12% was taken into account in the simulations to optimize the fitting results.

The ellipsometric spectra $\tan\Psi$ and $\cos\Delta$ of the NCD film are presented in Fig. 1 for several temperatures. The spectra show a well-defined interference pattern in the entire photon energy range, demonstrating the high transparency of the NCD film. At higher temperatures, the oscillator strength increases and the interference pattern shows a slight redshift.

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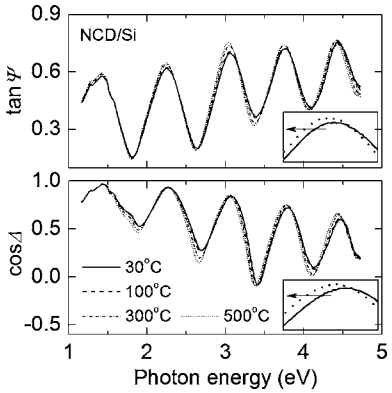

FIG. 1. Experimental ellipsometric spectra of the NCD film at different temperatures. Only the spectra obtained at 30, 100, 300, and 500 °C are presented for clarity. The insets show the enlarged redshift at 3.6–3.9 eV for 30 and 500 °C.

This effect may be ascribed to changes of the refractive index deriving from increasing structural disorder at elevated temperatures.[15,18] A strong thickness effect due to thermal expansion can be excluded due to the small expansion coefficient of diamond, the relatively small film thickness, and the limited temperature range studied.[4,12] In fact, it has been reported that the thermal expansion coefficient becomes less temperature dependent above 300 K for covalent semiconductor materials.[19] Therefore, the thicknesses of the NCD film of 310±5 nm and the SRL of 12±1 nm and the fraction of voids in the SRL were determined by fitting the 30 °C spectra and then used to fit the SE spectra at elevated temperatures.

The average value of the parameter E_0 is about 10.1±0.1 eV, indicating that the fundamental band gap is larger than the experimentally accessible high-energy limit of 4.75 eV. Note that the single-oscillator model describes the interband transition and corresponding subgap absorption by a broadening value.[20] No strong absorption features could be seen in the covered photon energy range, as expected for high-quality NCD films. The broadening parameter Γ is small, with a magnitude of about 0.37±0.01 eV. The absorption index κ is essentially independent of temperature with an estimated value of 7×10^{-3} at a photon energy of 2.0 eV. This absorption can be ascribed to electronic states introduced by sp^2 carbon bonds in grain boundaries (π,π^*), dangling bond states, distortions of tetrahedrally bonded carbon (σ,σ^*), and disorder induced band tailing (Σ,Σ^*) into the forbidden gap, as found by molecular-dynamics simulations.[21] Although SE measurements cannot separate different subgap transitions such as π-π^* or π-σ^*,[22] it can be concluded that π-π^* electronic transitions played a major role, due to the accumulation of sp^2 carbon bonds in the grain boundaries, detected by Raman spectroscopy.[10] For the present NCD films we find a substantially lower subgap absorption than previously reported for NCD,[14] as can be seen in Fig. 2 and Table I. Moreover, the results are compared with data of single-crystal diamond.

TABLE I. Parameter values of Eq. (2) for the NCD film. α is the optical absorption coefficient. The results of single-crystal diamond at the photon energies of 0.56 and 0.01 eV are taken from Refs. 3 and 4, respectively.

	Photon energy (eV)					
Parameters	0.01	0.56	1.20	2.00	3.00	4.50
$\alpha(\times10^3\ \mathrm{cm}^{-1})$	⋯	⋯	0.52	1.5	3.7	10.1
n_0	2.38	⋯	2.31	2.33	2.37	2.48
S_n	0.019	⋯	0.03	0.04	0.05	0.10
E_p	0.088	⋯	0.08	0.09	0.11	0.14
$\frac{1}{n}\frac{\partial n}{\partial T}(\times10^{-6}\ \mathrm{K}^{-1})$ (300 K)	3.2	6.7	6.5	6.1	5.2	3.6

The energy dependence of the refractive index n of the NCD film at different temperatures is presented in Fig. 3, indicating that the parameter A in Eq. (1) increases linearly with temperature. The refractive index increases substantially with photon energy, consistent with typical electronic transitions from the fundamental band gap. Moreover, the index of refraction increases only slightly with temperature and varies from 2.35 at 30 °C to 2.36 at 500 °C at the photon energy of 2.0 eV. This minute increase is due to increased electron-phonon interactions at elevated temperatures, making indirect transitions more probable.[19] The temperature dependence of the refractive index can be described by the well-known Bose-Einstein model

$$n(T) = n_0 + S_n\left[\frac{1}{\exp(E_p/kT)-1}+\frac{1}{2}\right]. \quad (2)$$

Here, n_0 is the refractive index towards 0 K, S_n is a dimensionless coupling constant, and k is the Boltzmann constant. The term $(\exp(E_p/kT)-1)^{-1}$ is the Bose-Einstein factor for an effective oscillator energy E_p that describes the vibrational degrees of freedom for $E_p \gg kT$.[4] Figure 4 gives the Bose-Einstein fit to the experimental refractive index at pho-

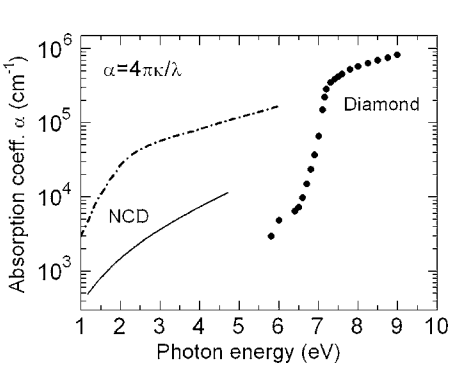

FIG. 2. Absorption coefficients of the NCD film determined from the measured absorption index in the subgap region (solid line). The dashed line presents results from Ref. 14. For comparison data of single-crystal diamond are also shown.

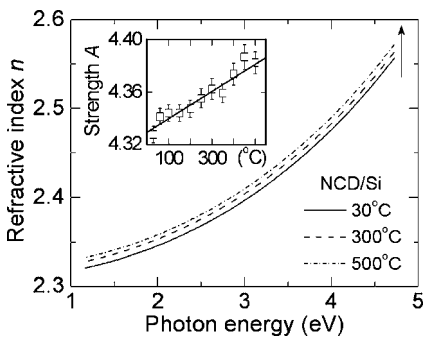

FIG. 3. Energy dependence of the refractive index of the NCD film is shown for 30, 300, and 500 °C. The inset shows that the fitted oscillator strength A of Eq. (1) increases linearly with temperature.

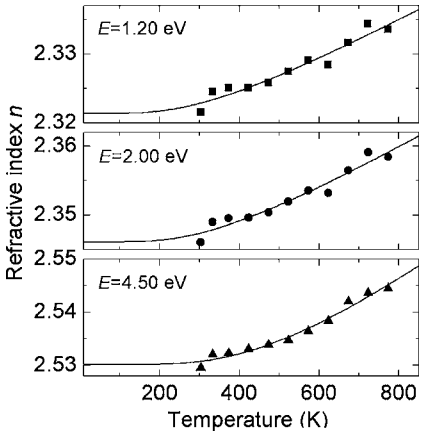

FIG. 4. Variation of the refractive index of the NCD film with temperature for the three photon energies of 1.20, 2.00, and 4.50 eV and the fit (solid lines).

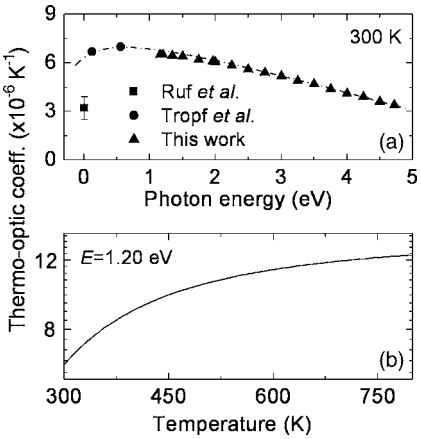

FIG. 5. Variation of the thermo-optic coefficient of the NCD film with photon energy at 300 K (a) and with temperature (b). Experimental results of single-crystal diamond are included for comparison in (a) (Refs. 3 and 4). The dashed line is a guide for the eyes.

ton energies of 1.2, 2.0, and 4.5 eV. For all photon energies, the Bose-Einstein model allowed a reasonable description of the temperature dependence, in particular, at the high-energy side. Note that the refractive index displays a dispersion behavior, unlike in the far-infrared region, where the refractive index remains constant and stays close to the long-wavelength value. Therefore, a large energy range from NIR to UV was taken into account in the present work to investigate the influence of temperature on the dispersion behavior. The parameter values of Eq. (2) are listed in Table I and increase slightly with photon energy, in agreement with the values of single-crystal diamond in the far-infrared region. This increase indicates that the coupling between phonons and electronic states at the valence and conduction band edges becomes more important at photon energies closer to the fundamental band gap,[18] as observed previously for other semiconductors, such as Si and GaAs.[19]

A thermo-optic coefficient of $(1/n)(\partial n/\partial T)=6.5\times10^{-6}$ K^{-1} was obtained for the NCD film at room temperature and the photon energy of 1.2 eV. This value is close to the data reported for bulk diamond at near-infrared and visible wavelengths [6.7×10^{-6},[3] 4.04×10^{-6},[11] and 5.12×10^{-6} K^{-1} (Ref. 13)]. As displayed in Table I and Fig. 5(a), there is a slight decrease of the thermo-optic coefficient at larger photon energies due to the contribution of higher energy transitions, which were not taken into account in the model. The variation of the thermo-optic coefficient at different photon energies is within scatter of experimental and theoretical data reported for single-crystal diamond. It can be expected that the different refractive indices of single-crystal and nanocrystalline diamond contribute to this discrepancy.[19] Correspondingly, the dispersion of the refractive index can affect the thermo-optic coefficient. On the other hand, the actual contents of sp^3 and sp^2 carbon bonds and disorder in the grain boundaries of the NCD film have a strong effect on the deviations from ideal single-crystal diamond.[10] Figure 5(b) shows the temperature dependence of the thermo-optic coefficient in the near-infrared region. Generally, the thermo-optic coefficient increases from 6.5×10^{-6} to 1.2×10^{-5} K^{-1} with temperature, in agreement with theory.[12,19]

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