

Thermal conduction in nanocrystalline diamond films: Effects of the grain boundary scattering and nitrogen doping

W. L. Liu, M. Shamsa, I. Calizo, and A. A. Balandin^{a)}

Nano-Device Laboratory, Department of Electrical Engineering, University of California–Riverside, Riverside, California 92521

V. Ralchenko, A. Popovich, and A. Saveliev

General Physics Institute of the Russian Academy of Sciences, 38 Vavilov Street, Moscow 119991, Russia

(Received 25 July 2006; accepted 7 September 2006; published online 26 October 2006)

The authors investigated thermal conductivity (K) in nanocrystalline diamond (NCD) films on silicon using the 3ω and laser flash techniques. The K temperature dependence has been studied for the undoped and nitrogen-doped NCD films for $T=80\text{--}400$ K and compared with that in microcrystalline diamond (MCD) films. The effects of phonon scattering from the grain boundaries and film interfaces on thermal conduction have been studied using three different models. For NCD the room temperature K is $0.1\text{--}0.16$ W/cm K and decreases with nitrogen doping. The K temperature dependence in NCD is different from that in MCD films and can be adequately described by the phonon-hopping model. © 2006 American Institute of Physics.

[DOI: 10.1063/1.2364130]

Diamond materials, owing to their unusual properties such as extreme hardness, chemical inertness, and high thermal conductivity, have been used for wear-resistive coatings, optical windows, surface acoustic-wave devices, and heat spreaders. To optimize the material properties, different growth technologies and types of diamond materials have been developed. Recently introduced nanocrystalline diamond¹ (NCD) attracted much attention for potential applications in electronics.² Synthesized by argon-rich microwave plasma assisted chemical vapor deposition process, NCD film can be grown with the grain diameter as small as $d\sim 2\text{--}5$ nm. Compared with faceted microcrystalline diamond (MCD), NCD films are smooth pinhole-free even for small ($\ll 1\ \mu\text{m}$) thicknesses. It has also been demonstrated that the electrical conductivity of NCD films can be changed by nitrogen (N_2) doping to form n -type material.³ These properties make NCD suitable for the proposed carbon-based electronics,⁴ in particular, with components made of carbon nanotubes. It may also be used in future downscaled complementary metal-oxide semiconductor technology.

Understanding thermal conduction in NCD films is important for applications in electronics and coatings. In its bulk form, diamond has the highest thermal conductivity (K) of all materials, which at room temperature (RT) is $K=10\text{--}22$ W/cm K depending on the quality.^{5–8} At the same time, only limited research has been done to understand thermal transport in NCD.⁹ Vlasov *et al.*¹⁰ investigated the thermal properties of the diamond-carbon composites ($d\sim 6$ nm) and obtained $K=0.003\text{--}0.017$ W/cm K at RT. Ahmed *et al.*¹¹ reported RT $K\sim 0.26$ W/cm K for their NCD. The previous studies did not establish temperature dependence, which is essential for understanding the dominant scattering mechanisms limiting K in NCD films.

In this letter we report the temperature dependent study of thermal conduction in the undoped and N_2 -doped NCD films. For comparison, we have measured K in chemical va-

por deposition (CVD)-grown MCD film. The measurements have been carried out using 3ω technique for $T=80\text{--}400$ K. In addition, the laser flash technique (LFT) has been used to study K dependence on N_2 -doping concentration at RT. To elucidate the role of the phonon-grain-boundary and phonon-film interface scattering, we evoked three different models. It is intriguing that K temperature dependence in NCD films is intermediate between that of crystalline and disordered materials and described very well by the phonon-hopping model. The latter suggests that K in NCD is limited by the properties of the grain boundaries in a wide T range.

The samples were grown on Si substrates in a microwave plasma CVD reactor (DF-100 model, 2.45 GHz). The MCD film of $3.4\ \mu\text{m}$ thickness and surface roughness $R_a=133$ nm, referred to as Poly, has been grown for 2 h with gas mixture 4% $\text{CH}_4/96\%$ H_2 at substrate temperature of $800\ ^\circ\text{C}$, pressure of 90 Torr, and microwave power of 4.3 kW. The NCD samples NCD_0 (film thickness of $2.2\ \mu\text{m}$), NCD_15 ($8.9\ \mu\text{m}$), and NCD_25 ($9.5\ \mu\text{m}$) were grown in the same CVD reactor using Ar-rich gas mixtures $\text{Ar}/(5\%)\text{H}_2/(2\%)\text{CH}_4/\text{N}_2$ with N_2 concentrations of 0%, 15%, and 25%, respectively (Ar was varied to balance) at following conditions: microwave power of 2.4 kW, pressure of 90 Torr, and substrate temperature of $800\ ^\circ\text{C}$. The average surface roughness R_a for the NCD is below 40 nm as measured by the atomic force microscopy (AFM) [see Fig. 1(a)]; no columnar growth features were seen in the film cross section [Fig. 1(b)]. The grain size d is 22–26 nm and $2\ \mu\text{m}$ for NCD [x-ray diffraction (XRD) data] and MCD films [scanning electron microscopy (SEM) data], respectively.

The sample postgrowth composition has been inspected using Renishaw Raman spectrometer. Figure 2 shows Raman spectra under 488 nm excitation. In MCD film the most prominent peak is at $1332\ \text{cm}^{-1}$, which corresponds to optical vibrations in sp^3 -bonded carbon atoms in the diamond crystal structure while a weak peak at $1500\ \text{cm}^{-1}$ is associated with sp^2 -dominant disordered carbon.^{12–14} The peaks observable in our NCD samples, i.e., 1140 and $1330\ \text{cm}^{-1}$, and the overlapping bulge from two peaks, 1450 and

^{a)} Author to whom correspondence should be addressed; electronic mail: balandin@ee.ucr.edu; http://ndl.ee.ucr.edu

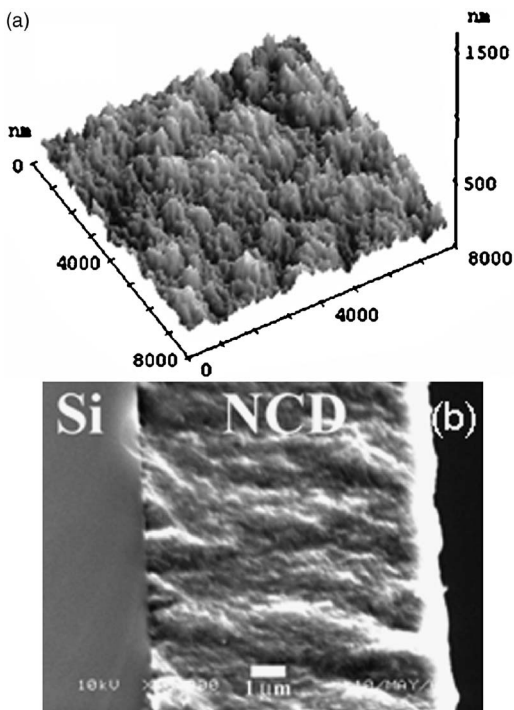


FIG. 1. (a) AFM image of the surface topography and (b) SEM image of the cross section of a typical nanocrystalline diamond film (sample with 25% N_2 doping). Surface roughness is $R_a=38.5$ nm.

1560 cm^{-1} , are characteristic for NCD. The peak of 1140 cm^{-1} is due to *trans*-polyacetylene at grain boundaries, while the peak at 1450 cm^{-1} represents the mixture of *a*-C with graphite content. The peaks at ~ 1330 and 1560 cm^{-1} are *D* and *G* bands, respectively. With the addition of N_2 , the intensity of *D* band decreases while the intensity of the *G* band increases accompanied by a shift to lower frequencies, which is in line with the theory¹³ and reported experimental data.¹⁴

The 3ω technique is based on driving ac through the metal heater line at frequency 1ω , which results in heating, measurable as a resistance change at the frequency of 3ω .^{15,16} Since doped NCD films were electrically conductive, we deposited 90-nm-thick SiN insulation layer on top surfaces. The Cr(10 nm)/Au(100 nm) metallic heater-thermometer wires with widths of 10 and $30\ \mu\text{m}$ were patterned on top of the insulation layer and fabricated by the

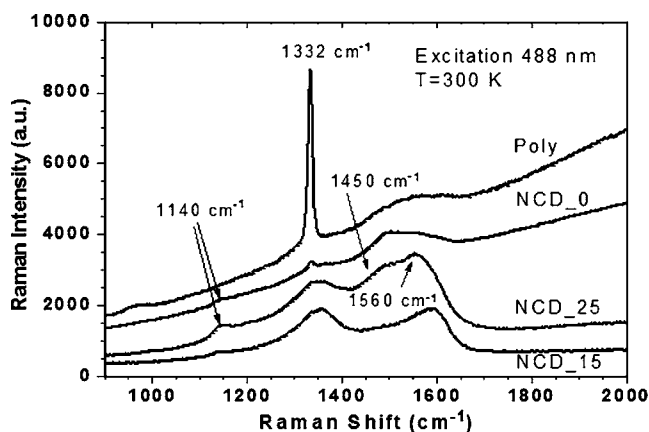


FIG. 2. Raman spectra from microcrystalline and three nanocrystalline diamond films.

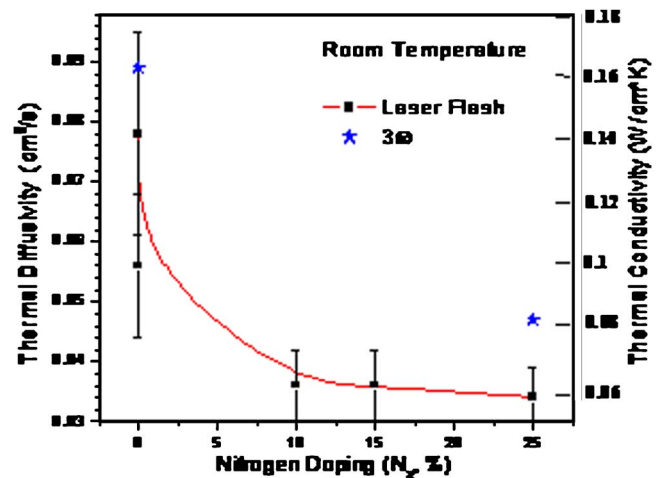


FIG. 3. Thermal conductivity of the nanocrystalline diamond films as a function of the nitrogen doping concentration measured by the laser flash technique (squares) and 3ω method (stars).

e-beam evaporation and lift-off. The measurements were conducted inside a vacuum cryostat. A numerical program based on the solution of the heat diffusion equations was developed to extract K values.¹⁶ LFT, used for RT study, is based on measuring traveling time of the thermal wave excited by a laser pulse, which determines the thermal diffusivity D . In these measurements a pulsed neodymium-doped yttrium aluminum garnet laser was utilized for heating the sample surface, while the temperature kinetics was monitored with the HgCdTe detector.¹⁰ The thermal conductivity was found as $K=D\rho C$, where ρ and C are the mass density and specific heat of the material, respectively. Figure 3 shows K of NCD with different doping levels obtained using two different methods at RT. In processing LFT data, we assumed $\rho=3.51\text{ g/cm}^3$ and $C=0.511\text{ J/g K}$, which correspond to crystalline diamond. 3ω method determines K directly and does not require ρ and C inputs. One can see that there is good agreement in K values obtained by these two techniques. The measured $K=0.1\text{--}0.16\text{ W/cm K}$ for undoped NCD is much smaller than the values for crystalline diamond. K reduces further with increasing doping due to stronger phonon scattering on point defects,¹⁷ reaching $\sim 0.06\text{ W/cm K}$ in 25% N_2 -doped film.

Figure 4 shows K as a function of temperature T for MCD film (Poly) and two NCD films NCD_0 (undoped) and NCD_25 (doped with 25% N_2). Unlike bulk crystals, MCD K - T behavior does not have a pronounced low- T peak and rolls off slower than $1/T$ around RT. These indicate that the phonon scattering from the film interfaces and grain boundaries play an important role at low T . The measured RT value for MCD sample is $K=5.51\text{ W/cm K}$. On the other hand, K temperature dependence of NCD samples is rather different, which suggests stronger grain boundary scattering. The monotonic K increase with temperature is similar to that in disordered materials. RT thermal conductivities for NCD samples is 0.16 and 0.08 W/cm K for the undoped ($d=22\text{ nm}$) and doped ($d=26\text{ nm}$) films, respectively, i.e., one to two orders of magnitude lower than those in MCD.

To explain K - T dependence for NCD and MCD films, we evoked three different theoretical models. The results of calculations are shown in Fig. 4 with solid lines. The curve for bulk diamond is calculated using Callaway's model,¹⁸ which is commonly used to describe phonon transport in

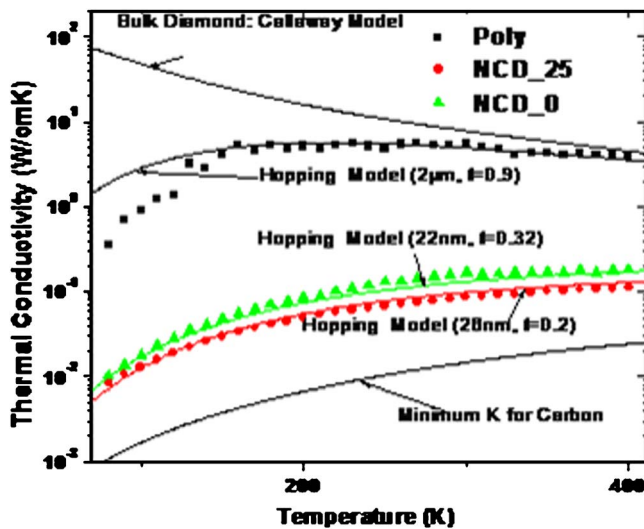


FIG. 4. Thermal conductivities as a function of temperature measured for microcrystalline (Poly) diamond and undoped (NCD_0) and nitrogen-doped (NCD_25) nanocrystalline diamond films. The solid lines are simulation results obtained using the Callaway, phonon-hopping, and minimum thermal conductivity models.

bulk crystals. In our calculations, we used bulk scattering parameters from Ref. 5. This curve presents the upper bound for K , which can be obtained in the crystalline diamond with given parameters without boundary effects on phonons. Substantial deviation of the Callaway-model curve from the measured data for MCD at low T suggests strong phonon scattering from the grain boundaries and substantial Kapitza thermal boundary resistance¹⁹ at the MCD film interfaces.²⁰

The low bound for K in carbon-based material is provided by the minimum thermal conductivity (MTC) approach based on Einstein's model for the specific heat and the assumption of the random walk between localized excitations in the disordered material.²¹ MTC model is conventionally used for disordered materials. One can see that the MTC gives K values, which are an order of magnitude below the measured data, which is reasonable since the grains in NCD are crystalline inside and the film is only partially disordered.

The theoretical approach, which gives the best agreement with the measured temperature dependence of thermal conductivity in NCD films, is the phonon-hopping model (PHM).²² PHM has been proposed for polycrystalline materials. It assumes that the phonon transport inside the grain follows "bulk rules" while the phonon transition from one grain to another, i.e., hopping, is characterized by the *transparency* parameter t . In general, t is obtained from fitting to experimental data, although in simplest cases it can be calculated from first principles.²² The best-fit PHM curves for the undoped NCD ($d=22$ nm) and MCD ($d=2$ μ m) were obtained with $t=0.32$ and $t=0.9$, respectively, while the best-fit curve for doped NCD ($d=26$ nm) was calculated with $t=0.2$. One can see an excellent agreement between the theory and experiment for NCD films. The smaller t value for the doped NCD can be related to the fact that nitrogen dopants cluster on the grain boundaries, which is in line with observations reported in Ref. 13. Accumulation of dopant atoms on the boundary and thicker grain boundaries composed of nondiamond carbon²³ reduces the boundary transparency and increases thermal resistance of NCD. It is interesting to note

that the effect of dopant clustering on K is somewhat offset by the fact that N_2 addition leads to increase in the grain size, which was observed earlier.¹³

Notable discrepancy of PHM predictions for MCD at low T can be explained by the Kapitza resistance at the film interfaces, which is not included in the model. Indeed, t parameter in PHM takes care of the thermal resistance at the grain boundaries but does not account for the resistance at the MCD/Si and MCD/insulator interfaces. In NCD films, the omission of the Kapitza resistance at the film interfaces does not show up because the total grain boundary scattering in NCD is much stronger than in MCD (since d is two orders of magnitude smaller). To sum up, the thermal properties of NCD are to the large degree determined by the grain boundaries and size over the large temperature range. In MCD films characterized by much larger grain size, the thermal Kapitza resistance at the film interfaces also plays an important role at low temperature.

The authors are thankful to E. Loubnin for XRD analysis of the NCD samples. The work at UCR was supported, in part, by MARCO Center on Functional Engineered Nano Architectonics (FENA), and NSF through an award to A.A.B. The work at GPI was supported by the Russian Ministry of Science and Education through Contract No. 02.445.11.7353.

¹D. M. Gruen, *Annu. Rev. Mater. Sci.* **29**, 211 (1999).

²W. S. Yang, O. Auciello, J. E. Butler, W. Cai, J. A. Carlisle, J. E. Gerbi, D. M. Gruen, T. Knickerbocker, T. L. Lasseter, J. N. Russell, L. M. Smith, and R. J. Hamers, *Nat. Mater.* **1**, 253 (2002).

³O. A. Williams, S. Curat, J. E. Gerbi, D. M. Gruen, and R. B. Jackman, *Appl. Phys. Lett.* **85**, 1680 (2004).

⁴T. Zimmerman, M. Kubovich, A. Denisenko, K. Janioschovsky, O. A. Williams, D. M. Gruen, and E. Kohn, *Diamond Relat. Mater.* **14**, 416 (2005).

⁵R. Berman, P. R. W. Hudson, and M. Martínez, *J. Phys. C* **8**, L430 (1975).

⁶A. V. Sukhadolau, E. V. Ivakin, V. G. Ralchenko, A. V. Khomich, A. V. Vlasov, and A. F. Popovich, *Diamond Relat. Mater.* **14**, 589 (2005).

⁷E. Woerner, C. Wild, W. Müller-Sebert, R. Locher, and P. Koidl, *Diamond Relat. Mater.* **5**, 688 (1996).

⁸J. E. Graebner, J. A. Mucha, L. Seibles, and G. W. Kammlott, *J. Appl. Phys.* **71**, 3143 (1992).

⁹D. M. Gruen, S. Liu, A. R. Krauss, and X. Pan, *J. Appl. Phys.* **75**, 1758 (1994).

¹⁰A. Vlasov, V. Ralchenko, S. Gordeev, D. Zakharov, I. Vlasov, and P. Belobrov, *Diamond Relat. Mater.* **9**, 1104 (2000).

¹¹S. Ahmed, R. Liske, T. Wunderer, M. Leonhardt, R. Ziervogel, C. Fansler, T. Grotjahn, J. Asmussen, and T. Schuelke, *Diamond Relat. Mater.* **15**, 389 (2006).

¹²W. L. Hsu, D. M. Tung, E. A. Fuchs, K. F. McCarty, A. Joshi, and R. Nimmagadda, *Appl. Phys. Lett.* **55**, 2739 (1989).

¹³S. Bhattacharyya, O. Auciello, J. Birrell, J. A. Carlisle, L. A. Curtiss, A. N. Goyette, D. M. Gruen, A. R. Krauss, J. Schlueter, A. Sumant, and P. Zapol, *Appl. Phys. Lett.* **79**, 1441 (2001).

¹⁴G. Z. Wang, F. Ye, C. Chang, Y. Liao, and R. C. Fang, *Diamond Relat. Mater.* **9**, 1712 (2000).

¹⁵D. G. Cahill, *Rev. Sci. Instrum.* **61**, 802 (1990).

¹⁶W. L. Liu and A. A. Balandin, *Appl. Phys. Lett.* **85**, 5230 (2004); *J. Appl. Phys.* **97**, 073710 (2005); M. Shamsa, W. L. Liu, A. A. Balandin, and J. L. Liu, *Appl. Phys. Lett.* **87**, 202105 (2005).

¹⁷J. Zou, D. Kotchetkov, A. A. Balandin, D. I. Florescu, and F. H. Pollak, *J. Appl. Phys.* **92**, 2534 (2002); *Appl. Phys. Lett.* **79**, 4316 (2001).

¹⁸J. Callaway, *Phys. Rev.* **113**, 1046 (1959).

¹⁹P. L. Kapitza, *J. Phys. (Moscow)* **4**, 181 (1941).

²⁰E. T. Swartz and R. O. Pohl, *Appl. Phys. Lett.* **51**, 2200 (1987).

²¹D. G. Cahill and R. O. Pohl, *Solid State Commun.* **70**, 927 (1989).

²²L. Braginsky, N. Lukzen, V. Shklover, and H. Hofmann, *Phys. Rev. B* **66**, 134203 (2002).

²³J. Birrell, J. A. Carlisle, O. Auciello, D. M. Gruen, and J. M. Gibson, *Appl. Phys. Lett.* **81**, 2235 (2002).