

Correlating optical absorption and thermal conductivity in diamond

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The presence of defects in diamond induces one-phonon infrared absorption which is not allowed in the perfect crystal due to symmetry. Concomitantly the thermal conductivity is reduced by additional phonon-defect scattering. For single crystal diamonds irradiated with fast neutrons, we find a correlation between the one-phonon absorption and the room-temperature thermal conductivity valid over three orders of magnitude in defect concentration. This relation holds for both unannealed and annealed crystals for which the detailed configuration of defects is different, as well as for a synthetic diamond film containing a similar type of disorder. Infrared absorption can thus be used to determine the thermal conductivity of diamonds containing vacancy-related defect centers.

The capability of producing diamond in the laboratory using chemical vapor deposition (CVD) techniques has paved the way for many technological applications of this material, ranging from infrared windows to high heat flux coatings. While the quality of CVD diamond has increased greatly in recent years, many of the most outstanding properties of this form of carbon, such as high thermal conductivity, low electrical conductivity, and high strength, have not been fully realized due to the presence of defects at fairly low levels of concentration. Most CVD diamond materials grown today contain many types of defects, including vacancies, nondiamond carbon, nitrogen, hydrogen, and metallic impurities. It must be stressed that even in low concentration, well below 1%, such defects can drastically degrade many of diamond's most useful properties. Because of the simultaneous occurrence of many types of defects, it is not always clear how each defect influences a given property. We have attempted to clarify this situation by studying single crystals of diamond into which certain defects are artificially introduced in a reasonably controlled manner. The method we have chosen is the introduction of vacancies and disordered carbon by irradiation of diamond single crystals with fast neutrons. The resulting defect morphology of irradiated diamond is in many ways similar to that of CVD films, and indeed, studies of the thermal conductivity of irradiated diamonds¹ indicate that the additional thermal resistivity due to defect scattering resembles that which occurs in the synthetic-vapor-grown material.^{2,3} In particular, in both CVD diamond and neutron-irradiated single crystal diamond, evidence suggests the existence of small but highly disordered regions of nondiamond carbon and vacancy complexes. A detailed but important structural difference between these two types of diamond is the existence of grain boundaries in the CVD material. As a result, the disordered regions in CVD diamond tend to occur on the surfaces of grains while in neutron-irradiated diamond the vacancy-rich disordered regions are uniformly distributed throughout the sample. In this letter we show, despite this subtle structural difference, the thermal conductivity of irradiated and CVD diamond scales with both the defect concentration and the

defect-induced one-phonon infrared absorption. These results indicate that for diamond materials containing vacancies and disordered carbon, the thermal properties can be reasonably well characterized by measuring the optical absorption.

It has previously been shown¹ that additional scattering of phonons occurs in irradiated diamond from clusters of defects of size $a \sim 10\text{--}15 \text{ \AA}$. The existence of such clusters is consistent with the observation of Prins⁴ of the presence of vacancy clusters on the order of this size in ion-implanted diamond. Such clusters have also been produced by electron irradiation and directly observed using transmission electron microscopy⁵ or inferred from thermal conductivity measurement.⁶ In our previous study of irradiated but unannealed diamond,¹ the thermal conductivity κ was measured from 7 to 300 K and was characterized by a dip in the curve at a temperature corresponding to the dominant phonon wave vector $q \sim a^{-1}$. For $a = 10 \text{ \AA}$ the dip occurs near 30 K. With increasing fluence the cluster size remained relatively unchanged but the number density of clusters increased. In this study we have extended this investigation to annealed crystals for which the defect size grows to nearly 100 \AA , causing the dip in κ to occur at even lower temperatures. For this reason, we have extended the thermal conductivity measurement to below 1 K using a dilution refrigerator. The samples used in this study were natural diamond single crystals. Sample 1 was irradiated to cumulative fluences of 3×10^{16} , 1.2×10^{17} , 6×10^{17} , and 4.5×10^{18} neutrons cm^{-2} and was reported in Ref. 1. Sample 2 was irradiated to a fluence of 4×10^{18} neutrons cm^{-2} and subjected to successive high vacuum anneals at 425, 800, and 1180 $^{\circ}\text{C}$ for 4 h each. The purpose of these anneals was to alter the defect configuration, since previous studies indicate that vacancy migration in diamond begins to occur near 600 $^{\circ}\text{C}$.⁷

Infrared spectra were gathered using a Nicolet spectrometer, and the absolute absorption was calibrated assuming an absorption coefficient of 12.3 cm^{-1} at 2000 cm^{-1} , near the center of the two-phonon intrinsic absorption band.⁸ The infrared absorption spectrum of an unirradiated diamond and that of diamond 2 prior to annealing

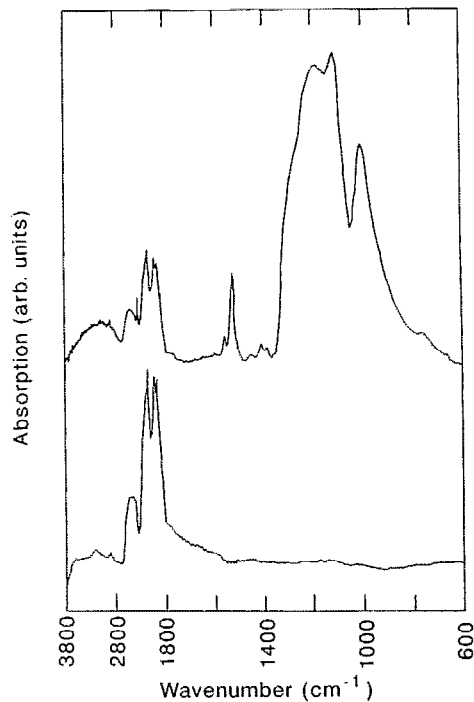


FIG. 1. Infrared absorption of unirradiated type IIa diamond (bottom) and diamond irradiated to 4×10^{18} neutrons cm^{-2} (top). The abscissa scale is nonlinear in order to emphasize the one-phonon region of the spectrum below 1330 cm^{-1} .

is shown in Fig. 1. For the unirradiated crystal, absorption occurs only above the Raman frequency (1332 cm^{-1}) because by symmetry absorption in the one-phonon region of the spectrum is disallowed.^{9,10} Upon irradiation a defect-induced one-phonon absorption is observed which scales with fluence.¹ The peak near 1200 cm^{-1} occurs not only in irradiated diamond but also in diamond containing large amounts of nitrogen, and thus is not a localized excitation due to a particular defect, but a lattice mode, and has been identified as arising due to the maximum in the density of states of the LO-phonon mode.¹¹

Figure 2 shows the thermal conductivity of sample 1 as a function of temperature. The dip in the curve near 30 K is clearly visible and grows stronger with increasing fluence. The attribution of this dip to scattering by agglomerates as opposed to another type of interaction, e.g., resonance scattering, has been previously discussed.¹ The solid lines are fits to the data assuming standard forms for Umklapp, point-defect, and boundary scattering,¹² as well as a scattering rate due to agglomerates of vacancies. This rate is of the form⁶

$$\begin{aligned} \tau^{-1} &= \rho_i v \pi a^2 / 4 \quad \omega > v/a \\ &= \rho_i \pi a^6 \omega^4 / 4v^3 \quad \omega < v/a \end{aligned}$$

where ρ_i is the number density of clusters and a is the cluster size; ω and v are the phonon frequency and velocity, respectively. Thus the thermal conductivity can be used as a kind of crude but effective spectroscopy of the concentration and spatial extent of the defective regions. Figure 3 shows data for the annealed sample 2. It can be seen that

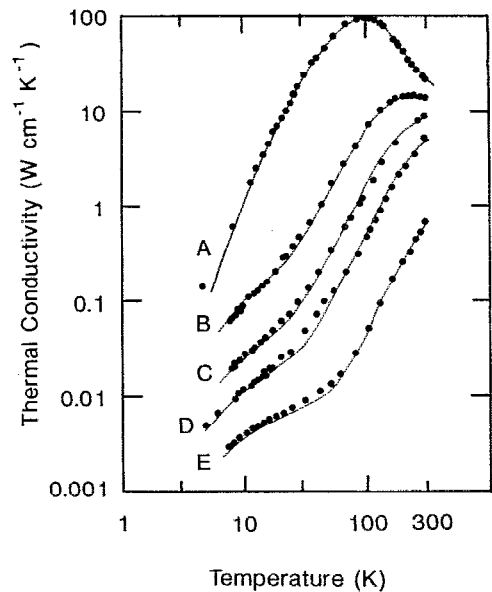


FIG. 2. Thermal conductivity of diamond irradiated with fast neutrons. Curve A: unirradiated; curve B: 3×10^{16} neutrons cm^{-2} ; curve C: 1.2×10^{17} neutrons cm^{-2} ; curve D: 6×10^{17} neutrons cm^{-2} ; curve E: 4.5×10^{18} neutrons cm^{-2} . Solid lines are fits to the data discussed in the text.

the dip shifts to lower temperature upon annealing. Interestingly, the dip seems to be most pronounced for the 800°C anneal. This effect occurs because the dips in the unannealed and 425°C samples occur at slightly higher temperature and are partially masked by point-defect scattering, while the dip in the 1180°C sample occurs at a lower temperature and is partially masked by boundary scattering. In essence, the 800°C anneal produces a defect size which maximizes the agglomerate scattering at a temperature (approximately 8 K) where both boundary scat-

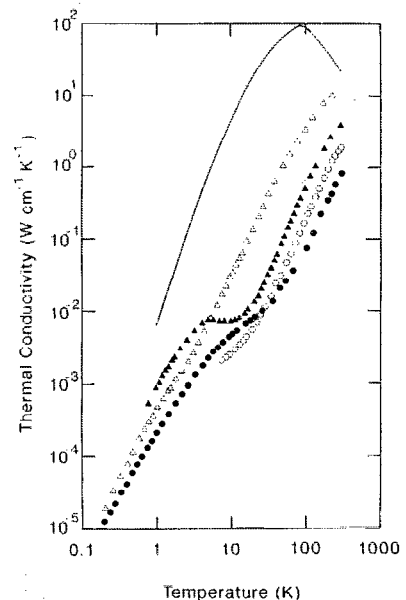


FIG. 3. Effect of annealing on the thermal conductivity of diamond irradiated to 4×10^{18} neutrons cm^{-2} . Symbol designation: (●): unannealed; (○): annealed at 425°C ; (▲): annealed at 800°C ; (△): annealed at 1180°C . Solid line: unirradiated diamond.

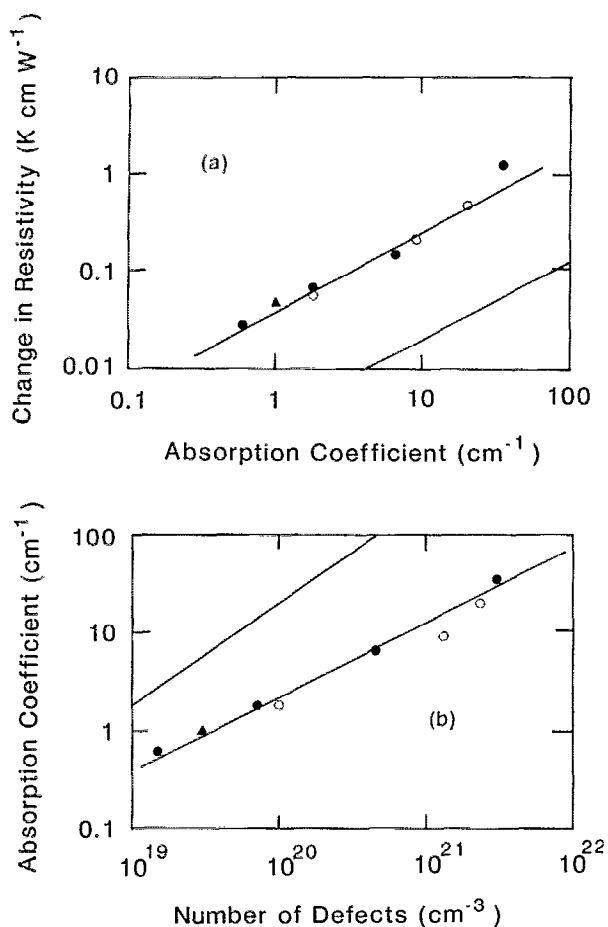


FIG. 4. (a) Change in the room-temperature resistivity vs absorption coefficient at 1200 cm^{-1} and (b) absorption at 1200 cm^{-1} vs total defect concentration determined from thermal conductivity. Symbol designation: (●): irradiated and unannealed single crystals; (○): irradiated and annealed single crystals; (▲): synthetic diamond film. Solid lines represent the resistivity/absorption (Ref. 13) and absorption/concentration (Ref. 14) relationships for nitrogenous defects.

tering and point-defect scattering are relatively weak. After the final anneal the dip is very weak and occurs near 3 K, corresponding to a defect size of approximately 100 \AA . From the fit to the data of Figs. 2 and 3 we determine ρ_t and α , and, assuming that the disordered region is spherical, we can determine the total number of defect atoms N_d .

Upon an increase in irradiation the defect-induced one-phonon absorption increases in intensity,¹ and then decreases again as the crystal is annealed. This observation, together with the fact that the room-temperature conductivity of the sample is partially recovered upon annealing (see Fig. 3), suggests that at least a portion of the damage created by irradiation is removed by the heat treatment. The most likely avenue for a decrease in total defect concentration is vacancy/interstitial recombination. Another effect of the annealing process is the growth of cluster size and decrease of cluster density. Evidently, annealing not only induces partial vacancy/interstitial recombination but also causes vacancy clusters to coalesce into larger regions of disorder.

A plot of the change in the room-temperature thermal resistivity (with respect to that of the unirradiated crystal)

as a function of the absorption coefficient at 1200 cm^{-1} is shown in Fig. 4(a). Figure 4(b) shows the dependence of the absorption coefficient on the total defect concentration N_d determined from the thermal conductivity. Included in this figure are data corresponding to a diamond film containing a small amount of sp^2 -bonded carbon.² It is interesting to note that despite the very different configuration of defects in unannealed and annealed samples (defect sizes ranging from 10 to 100 \AA) and in a diamond film (defects occurring at the grain boundaries), the relation between absorption at 1200 cm^{-1} , thermal resistivity, and defect concentration shown in Fig. 4 still holds. Figure 4 also shows the well-known relationships between thermal resistivity and optical absorption due to nitrogenous defects¹³ and nitrogen content vs optical absorption at 1200 cm^{-1} .¹⁴ For a given concentration, nitrogen provides about a factor of 10 larger optical absorption than the vacancy-related defect centers in the irradiated material. This is due to the stronger dipole moment of the nitrogen atom in the diamond lattice compared to the vacancy. In fact, if one assumes that the optical absorption is proportional to the square of the dipole moment, the results of Fig. 4 indicate that the dipole moment of the vacancy in diamond is only about one-third that of a nitrogen atom.

To summarize, we have correlated the one-phonon optical absorption in diamond containing vacancy-related defects with the defect concentration and the room-temperature thermal conductivity. These relations seem to hold for CVD diamond also. The results thus indicate that one can characterize the thermal properties of these technologically very important materials by measurement of the optical absorption.

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