Optical and Electronic Properties of Diamonds

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Abstract

Diamond shows interesting optical and electronic properties. Absorption and emission exist at energies well below the gap energy of around 5.6 eV even in the most perfect diamonds due to lattice defects. Because there is intense emission in the blue and green regions, diamonds can be used as scintillation detectors of ionizing radiation. The presence of defects causes some diamonds to be semi-conductors. Because of their high thermal conductivity at room temperature, such semi-conductors can be used as thermistors.

Diamonds are interesting to study due to their optical and electrical properties. Perfect diamonds have a band gap of approximately 5.6 eV; however, diamonds with defects will narrow the band gap considerably. The presence of these defects accounts for optical emission and absorption at visible wavelengths, and for much lower resistivities than would be expected for a perfect diamond; in fact, some diamonds are like semiconductors with resistivities on the order of a few ohm-cm.

Due to optical emission at visible wavelengths, diamonds can be used as scintillation detectors. Semi-conducting diamonds make useful practical thermistors due to their very high thermal conductivity. There is still much research to be done in order to effectively utilize the capabilities of diamonds; in particular, to cost-effectively produce synthetic diamonds with the desired properties.

DIAMOND STRUCTURE

The diamond structure consists of two interlaced fcc structures of carbon atoms with relative positions of (0,0,0) and (1/4,1/4,1/4). The lattice constant a=3.56 Å. This arrangement yields tetrahedral bonding between nearest neighbor atoms with a bond length b=1.53 Å. The bond is a covalent bond with sp-3 hybridization.

OPTICAL PROPERTIES OF PERFECT DIAMONDS

Because the gap energy is around 6 eV for a perfect diamond, there would be expected to be no optical absorption nor stimulated emission for wavelengths longer than ultra-violet (about 2000 Å). In practice, there exist 'water-white' diamonds, but also diamonds with different colors under white light, including pink, blue, yellow, and green, which happens due to the absorption of certain wavelengths, thus causing the diamond to appear the corresponding complementary color. It is evident therefore that many diamonds have electronic band separations with energies much less than 6 eV.

Diamonds are classified as 'type 1' and 'type 2' depending on whether significant absorption occurs at wavelengths shorter than approximately 3000 Å or 2200 Å, respectively. A type 2 variety corresponds better to the theoretical prediction for a perfect diamond stated above. Figure 1 shows the absorption spectra of two type 2 diamonds at room temperature. There is some small absorption at low energies, but a very sharp increase in the absorption coefficient at around 5.4 eV or so, which corresponds to the theoretical prediction.

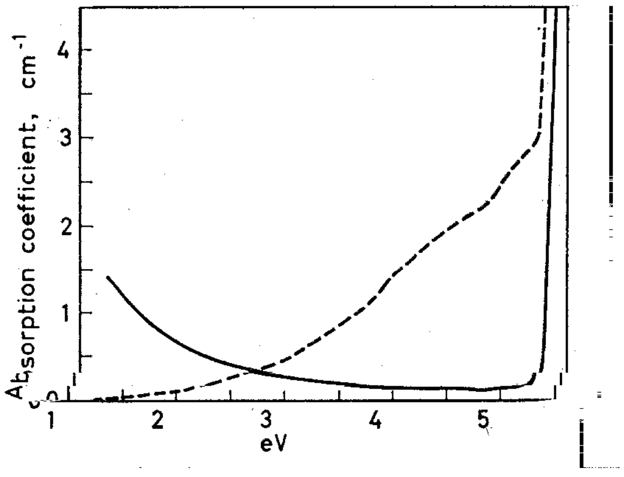

Figure 1: *Absorption spectra at room temperature of two type 2 diamonds.[2]*

Intense optical emission from diamonds may be stimulated by ionizing radiations such as X-rays, fast electrons, or alpha- particles. For even the most perfect type 2 diamonds, as shown in Figure 2, the emission is largely confined to a broad blue band, whose peak shifts to shorter wavelengths at lower temperatures. These results are in sharp contrast to the theoretical prediction, since, for perfect diamond, the only possible emission is with energy E_G approximately 5.6 eV (corresponding to a wavelength of approximately 2200 $\mathring{A}$). For the most perfect diamonds, the concentration of defects is only around a few parts per million. Even so, this small concentration of defects is sufficient to noticeably affect the emission peaks.

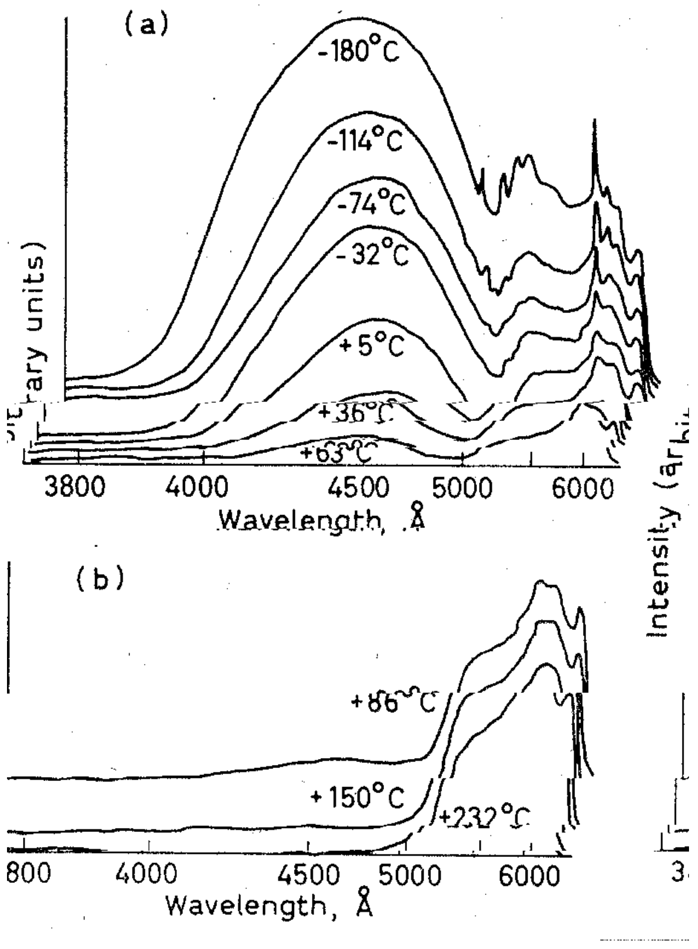

Figure 2: *Cathodoluminescence spectrum at different temperatures for a type 2 diamond.[3]*

OPTICAL PROPERTIES OF DIAMONDS WITH DEFECTS

After many specimens of diamond were examined, the distinction made between 'type 1' and 'type 2' diamonds due to whether there was significant absorption at wavelengths longer than 2200 $\mathring{A}$ was shown to be inadmissible, as there was a variety of different 'cut-off' wavelengths. It was therefore concluded that the difference was arbitrary and simply due to the relative proportion of defects in the diamonds. This fits in with the prediction that for diamonds with defects the electronic separation between levels will be less than 5.4 eV; how much less depends on the proportion of defects.

Figure 3 shows a variety of emission spectra for natural diamonds. It can be seen that the wavelengths are approximately between 4000 and 7000 Å, and that the spectrum is highly specimen dependent. It is interesting that the range of emitted wavelengths is similar for the most perfect diamonds and for the more imperfect ones, although the shapes of the spectra are different.

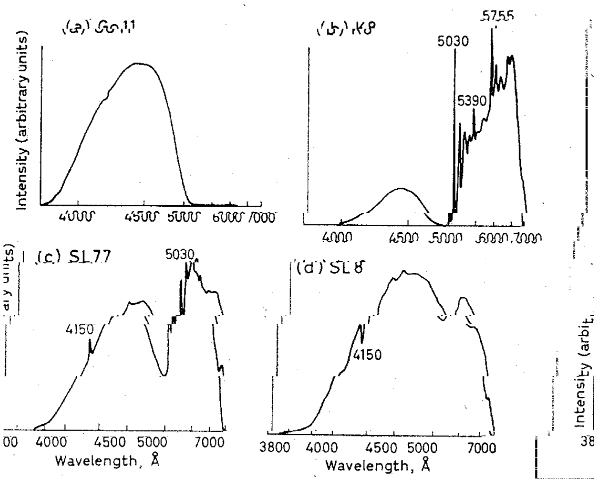

Figure 3: *Cathodoluminescence spectra for four specimens of natural diamond.[3]*

DIAMONDS AS SCINTILLATION DETECTORS

As shown above, de-excitation transitions at defect levels causes the emission of light at visible wavelengths, in the blue or green part of the spectrum, and this behavior is present in all diamonds. The intensity of this behavior has been shown to rarely differ by as much as a factor of 10, even among specimens with markedly different electrical and optical properties, and this intensity is more than sufficient to allow detection of any individual ionizing radiation of more than a few KeV by collection with a photomultiplier tube. After comparing α- and β- particle scintillation and cathodoluminescent spectra it was found that:

1) for β-particles the absolute magnitude was approximately proportional to the energy, and that the shape did not change with change in the energy;

2) the shape of the spectrum was almost completely specimen- independent for α-particles, whereas for β-particles a greater relative proportion of defects produced relatively more long-wavelength emission.[1]

ELECTRICAL PROPERTIES OF DIAMONDS WITH DEFECTS

Since diamond has the same crystal structure as germanium and silicon, many of the electrical properties of diamond can be predicted. Solid state theory gives the following formula for the number of negative carriers per unit volume, n:

$$n = 2\left(\frac{2\pi m_n kT}{h^2}\right)^{\frac{3}{2}} e^{\left(\frac{-(-E_C-E_F)}{kT}\right)}$$

where m_n is the effective mass of the negative carrier, E_C and E_F are the energies of the conduction level and the Fermi level, respectively, and $(E_C - E_F)$ is approximately equal to $E_G/2$ where E_G is the energy gap between the bottom of the conduction band and the top of the valence band. A similar expression will hold for the number of positive carriers (holes in the valence band) per unit volume, p, with m_n replaced by m_p, the effective mass of the hole, and (E_C- E_F) replaced by (E_F-E_V), where E_V is the energy level of the top of the valence band, and again, (E_F-E_V) is approximately equal to $E_G/2$. If we define the mean number of carriers, N, as equal to $\sqrt{np}$, and insert E_G=5.6 eV into the above expressions, there are less then 10^{-60} intrinsic carriers per unit volume at room temperature. Since the mobilities of the carriers for diamond would be expected to be of the same order of magnitude as for germanium, and since the resistivity, ρ, is approximately inversely proportional to N, we can estimate the resistivity of diamond by comparing with the values for germanium: (N=2.4 X 10^{13},ρ is on the order of $10^{2}\Omega$-cm), and thus the resistivity of a perfect diamond is expected to be above $10^{70}\Omega$-cm.

In practice, however, the resistivity of real diamonds rarely exceeds 10^{18} Ω-cm, and in fact may be as low as a few Ω-cm in semi-conducting diamonds. This fact further indicates that there are electronic levels in real diamonds with separations much less than E_G due to defects in the lattice, and that the resistivity decreases as the relative proportion of defects increases.

SEMI-CONDUCTING DIAMONDS

Certain aspects of a few specimens of semi-conducting diamonds have been studied and their general characteristics are similar to those of other impurity-activated semiconductors of low impurity concentration. They may show pronounced macroscopic inhomogeneities. They are often colored, as the lattice defects responsible for the semiconducting properties may also result in optical absorption at visible wavelengths, as discussed above.

By performing a Hall effect experiment, the sign of the predominant charge carriers may be determined. In the case of diamond, the carriers have been found to be of p-type (the charge carriers are positive holes travelling in the valence band). From the equation previously given for the number of charge carriers, the activation energy can be found by plotting ln T vs. 1/T; it is found to be 0.35 eV. The simultaneous measurement of the Hall constant and the resistivity allows the carrier mobility to be determined as about 1550 $\frac{cm\,sec^{-1}}{V cm^{-1}}$. This value agrees within experimental error with that found in several determinations by other methods.[4] The mobility as a function as temperature is approximately proportional to $T^{\frac{-3}{2}}$ which indicates that lattice scattering predominates. At room temperature n_p is approximately 2 X 10^{13} cm^{-3}, which is about the same as the intrinsic carrier density of germanium.

Semi-conducting diamonds, because of their high thermal conductivity, show a strong coupling between the charge carriers and the lattice vibrations. This coupling is known as phonon drag. An electric field drags the electron distribution from equilibrium, and then due to interaction between electrons and phonons, this is communicated to the long wavelength phonon modes. Since the phonon-phonon interaction is very small, the long wavelength phonon distribution is pushed far from equilibrium, creating a large heat current. Due to the high Debye temperature of diamond, this effect is appreciable even at room temperature, thus making semi- conducting diamonds useful practical thermistors.[1]

References

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