Evidence for Hopping Transport in Boron-Doped Diamond

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Electrical resistivity results were obtained from boron-doped natural and synthetic diamond over the temperature interval from 88 to 293°K. Resistivities ranged from $\gg 10^{14}$ Ω-cm for undoped diamond to 10^{-2} Ω-cm for "heavily" doped diamond. Analysis of the activation energies, obtained from the temperature dependency of the resistivity, indicate anomalous behavior. The tentative model, proposed to explain the results, is based on the impurity-level conduction scheme of Mott for compensated semiconductors.

MEASUREMENT of the temperature dependence of the resistivity of synthetic and natural diamond, doped with various impurities, was undertaken to determine the "activation energy" for conduction. Such activation energies may prove useful in defining the behavior of impurities in diamond. Conductivity results have previously been given for the type IIb (semiconductor) diamond by Wedepohl,[1] Bate and Willardson,[2] and Austin and Wolfe.[3] More recently, results have been given for normal type I and IIa (insulator) diamond by Pogodaev.[4]

On the basis of the usual hydrogenic model, the activation energy for boron-doped diamond may be estimated from U/K^2, where U is the ionization energy and K is the dielectric constant for diamond. Using the correction for the effective mass suggested by Wedepohl,[1] $m^*=0.25m_e$, would result in an estimated activation energy of 0.10 eV. This value is slightly higher than the largest of the many experimental values obtained.

Experimental determination of the "activation energy" was undertaken using a conventional "guillotine" probe and Keithley electrometer. Cooling of the crystals was accomplished by using liquid-nitrogen cooled nitrogen gas. The crystals used were all smaller than 800 μ with an average size of perhaps 350 μ.

For comparison purposes, results were obtained on a IIb stone and on small undoped type I and IIa crystals. The results obtained were in agreement with the results of Wedepohl[1] and Pogodaev[4] with the exception that the activation energy for synthetic crystals (measured at elevated temperatures) was higher (4.8 eV) than that reported for natural diamond by Pogodaev ($\sim$2.4 eV).[5] The former value appears to be close to the intrinsic gap for type I crystals.

The results of boron-doped diamond were obtained from both natural and synthetic crystals which were either diffusion doped and/or grown doped at pressures in the range of 55 kilobars to 70 kilobars. The pressures and temperatures were, in general, maintained in the diamond stable region of the equilibrium diagram. The crystals were unclassified as to diamond type, perfection, chemical composition, and inhomogeneity. The very high impedance of the undoped diamond, however, suggests that these factors, with the exception of compensation by otherwise nonconducting (nitrogen) donors,[6,7] may not significantly affect the results.

The resistivities encountered in the present work vary from $\sim 10^{20}$ Ω-cm (extrapolated to 293°K) for undoped diamond to 10^7 to 10^{-2} Ω-cm for boron-doped diamond. The behavior of the boron-doped crystals from ambient to liquid nitrogen temperature may be broadly subdivided into three groups:

I. Linear behavior in $\ln p$ vs $1/T$°K;

II. Nonlinear, slightly concave upward behavior, similar to that of boron-doped silicon (rare);

III. Linear behavior with change in slope at 0.0053 $1/T$°K.

The activation energies determined from the slope of $\ln p$ vs $1/T$°K are given in Table I. Nearly thirty discrete activation energies have been observed ranging from $E=0.0029$ eV to a value of $E=0.087$ eV. It was observed that doping at higher pressure (and temperature) favors lower activation energies with crystals doped at $\sim$70 kilobars being "degenerate." A surprising aspect of the activation energies is the tendency to form a series as indicated by the assignment of the number "n," where $n=1$ corresponding to 0.00144 eV is suggested.

The activation energies of boron-doped diamond are also apparently independent of the magnitude of the resistivity. Thus, low activation energies can occur for high-resistance crystals and vice versa.

The agreement of the activation energy estimated from the hydrogenic model with the higher activation energies of Table I is probably fortuitous. For the usual model to apply,

$$\rho^{-1}=neu_h,$$

$$n=2(2\pi m^* kT/h^2)^{3/2}e^{-E/kT}.$$

For spherical energy surfaces,

$$u_h=K/(m^{*5/2}T^{3/2}).$$

[1] P. T. Wedepohl, Proc. Phys. Soc. (London) **B70**, 177 (1957).
[2] R. T. Bate and R. K. Willardson, Proc. Phys. Soc. (London) **74**, 363 (1959).
[3] I. G. Austin and R. Wolfe, Proc. Phys. Soc. (London) **B69**, p. 329 (1956).
[4] K. N. Pogodaev, Soviet Phys.—Solid State **2**, 1317 (1961).
[5] These values are given in terms of 2 $kt/\ln p$; all others are in terms of $kt/\ln p$.
[6] W. V. Smith, P. P. Sorokin, I. L. Gelles, and G. J. Lasher, Phys. Rev. **115**, 1546 (1959).
[7] R. J. Elliott, Proc. Phys. Soc. (London) **76**, 787 (1960).

Thus, the temperature dependency should be determined by the "activation energy." Experimentally, a $T^{-3/2}$ temperature dependency for hole mobility has been reported by Redfield[8] for the insulating type I and IIa diamond.

The present results show that the experimentally determined activation energies in Table I are less than the value of $kT=0.026$ eV for 293°K. It would be expected, therefore, that the hole concentration should be essentially constant from thermal excitation and all crystals would be degenerate. Yet an activation energy is clearly observed and shows "linearity" in the plotted $\ln p$ vs $1/T$.

It would appear, on the basis of (a) E being generally less than kT, (b) the magnitude of p being independent of E, (c) the linear behavior of $\ln p$ vs $1/T$ indicating lack of complication by any unusual power law of u_h vs T, and (d) the observed multiplicity, that the observed activation energy is independent of the carrier concentration, being more probably related to the mobility.

A model has been suggested by Mott[9] in which an activation energy should be observed in the mobility for charge transport between impurity centers in compensated semiconductors. The model is applicable when the donor concentration is greater than the acceptor concentration and leads to conduction by hopping transport of holes between donor centers. At large separations, with little overlap of wave functions between centers an activation energy would appear to be necessary for the mobility.

Nitrogen has been found by Kaiser *et al.*[10] to be present in (type I) diamond in amounts up to 0.1%. Similar results are obtained for synthetic diamond. Recent spin resonance results[6] show that the nitrogen is substitutional with its excess electron located in an antibonding arbital where it does not give rise to conduction but may be available for compensation.[7] Thus at low temperatures the boron acceptor levels will be filled, producing N_A holes at the nitrogen donor level. Since the nitrogen level lies considerably above the boron level,[11] thermal effects will be negligible and the carrier concentration, i.e., holes in the nitrogen level, will be constant.

Excitation of an electron from the boron level to the nitrogen level would create and annihilate a hole simultaneously, producing little or no change in conductivity except through the difference in mobility of the levels. The boron-doped crystals are insensitive to ultraviolet irradiation.

A further consequence of the impurity conduction scheme, leading to hopping transport, is that it may take place via low-lying excited states.[12] Thus, the scheme may also account for the multiplicity of activation energies observed.

The present interpretation would tend to corroborate the conclusion that the common type I diamond contains nitrogen, which upon doping with boron acceptors almost certainly produces compensation. The rare type IIa and rarer IIb are comparatively nitrogen free with the latter containing an excess of uncompensated acceptor centers which produce its semiconducting properties.

TABLE I. Activation energies for boron-doped diamond.[a]

n	E_n (eV)	Typical values for E (eV) observed				f^*
1	0.00144	0.0016				1
2	0.00288	0.00293	0.00298			4
3	0.00432	0.00443	0.00432	0.00432	0.0042	6
4	0.00575	0.00572	0.00565	0.0060	0.00584	6
5	0.00720	0.0071	0.0071	0.00695	0.00707	10
6	0.00863	0.0083	0.0086	0.0086		6
7	0.0102	0.010	0.0099	0.010	0.0103	6
8	0.0115					0
9	0.0129	0.0127				1
10	0.0144	0.0143	0.0143	0.0144	0.0145	10
11	0.0158	0.0161				1
12	0.0173	0.0175	0.0174			2
13	0.0187	0.0185	0.0182			3
14	0.0202	0.0207				{1
15	0.0216	0.022	0.0218	0.022	0.213	{7
16	0.0230	0.0228				
17	0.0245	0.0243				1
18	0.0259	0.0263				1
19	0.0273	0.0278				{2
20	0.0288	0.0286	0.0292	0.0285	0.0283	{8
21	0.0303	0.0304	0.0307			{3
22	0.0317	0.032				1
23	0.0331	0.033				1
24						
27	0.0389	0.0394	0.039	0.0392		6
30						
		0.048	0.046			2
40	0.057	0.054	0.057			2
50	0.072	0.070	0.070			2
60	0.086	0.087	0.087	0.085		5

[a] f^* = Number of times observed, including reruns of the same crystal. Reruns do not necessarily yield the same activation energy. Some "half-integral" values were observed up to $n=10$. The uncertainty between levels increases with increasing energy (slope of $\ln p$ vs $1/T$). Note that the most common values appear to be grouped at $n=5$, 10, 15, etc.

[8] A. G. Redfield, Phys. Rev. **94**, 526 (1954).
[9] N. F. Mott, Can. J. Phys. **34**, 1356 (1956).
[10] W. K. Kaiser and W. L. Bond, Phys. Rev. **115**, 857 (1959).
[11] R. R. Urban, H. J. Logie, F. R. N. Nabarro, Proc. Phys. Soc. (London) **78**, 256 (1961).
[12] C. Herring, *Advances in Semiconductor Science* (Pergamon Press, New York, 1959), p. 543.