7. CONCLUSION

A microwave experiment has been suggested for obtaining the components of the conductivity tensor under hot electron conditions in n-type germanium. It is found that it would be possible to determine the carrier repopulation with good accuracy and also to obtain a definite indication about the population of the $\langle 100 \rangle$ valleys from a theoretical analysis of the obtainable data. In regions where the $\langle 100 \rangle$ valleys are not populated, the available data may be used for determining the anisotropy factor (K) under hot electron conditions.

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Electrical-Transport Measurements on Synthetic Semiconducting Diamond

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Four-probe electrical-conductivity measurements have been made on a series of General Electric aluminum-doped and nominally boron-doped synthetic semiconducting diamonds in the temperature range 223 to 323°K, and the results compared with those obtained from a natural semiconducting diamond (type IIb). These results, together with those obtained from optical-absorption, recombination-radiation, and chemical-impurity measurements on the same set of specimens, show that the same acceptor center, namely aluminum, is responsible for the semiconducting properties of both natural diamond and synthetic semiconducting diamond presently available. The large range of activation energies reported by other workers is considered to be due to the onset of impurity conduction at progressively higher temperatures with increasing concentrations of neutral acceptor centers.

INTRODUCTION

ELECTRICAL-transport,[1–6] optical-absorption,[7] and extrinsic recombination-radiation measurements[6] on natural semiconducting diamonds (type IIb) have shown that the semiconducting properties can be explained in terms of one definite invariant acceptor center with an activation energy of ~0.37 eV. This acceptor center has been identified with substitutional trivalent aluminum by comparing acceptor concentrations derived from Hall data with aluminum concentrations measured by neutron-activation analysis.[6] The analysis of the Hall-effect data indicates partial compensation of the acceptor concentration by deep-lying donors, with compensation ratios varying typically between 0.03 and 0.3.[2] The donor center is thought to be nitrogen at isolated substitutional sites with a donor binding energy of ~4 eV.[8]

The extrinsic features in the recombination-radiation spectra of natural semiconducting diamonds have been associated with the decay of excitons bound to the neutral acceptor center.[6] The recombination-radiation spectra obtained from both aluminum-doped and nominally boron-doped semiconducting synthetic diamonds[9] are virtually identical with those obtained from natural semiconducting diamond, except that the intensity of the extrinsic features relative to the intrinsic features is much stronger in the synthetic specimens.[6] These results suggest that the same acceptor center, namely aluminum, is responsible for the semiconducting properties of both natural and synthetic diamonds presently available, independent of the nominal dopant in the latter. Recombination-radiation measurements on more recent batches of semiconducting synthetic diamond,[9] including nominally undoped, boron-doped, and aluminum-doped specimens prepared using various catalysts, confirm this general picture.[10] Infrared-absorption measurements have also been made on a selection of aluminum-doped and nominally boron-doped synthetic diamonds.[11] The features in the line spectra associated with

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TABLE I. Summary of aluminum-impurity analyses on aluminum-doped and boron-doped semiconducting diamond.

Diamond description	Weight analyzed	Al concentration (ppm)
Al-doped diamond GECAL 1	350 (μg)	174±11
B-doped D1002 series (Color-selected batches)		
Yellow/white	1.9 (mg)	98±12
Pale blue	4.9 (mg)	133±11
Very dark blue	30.9 (mg)	138± 9

excited states of the acceptor center are identical with those observed in natural semiconducting diamonds,[7] except for line-broadening effects produced by the much higher acceptor concentrations in synthetic diamonds. The presence of aluminum in high concentrations in both aluminum-doped and boron-doped synthetic diamonds has been confirmed by neutron-activation analysis, and the results of these measurements are summarized in Table I. The experimental techniques involved have been described elsewhere.[12]

Electrical-transport measurements on doped synthetic diamonds have been reported by Wentorf and Bovenkerk[13] and by Wilson.[14] Wentorf and Bovenkerk made two-probe electrical conductivity measurements between 273 and 713°K on a selection of boron, aluminum, and beryllium-doped synthetic diamonds. Their specimens were all found to be p-type semiconductors, and activation energies for excitation of holes into the valence band were derived by plotting ln(resistivity) versus reciprocal temperature. The aluminum-doped crystals which were colorless or pale yellow-green generally exhibited activation energies ~0.32 eV, boron-doped specimens were predominantly blue in color with activation energies in the range 0.17–0.18 eV, and beryllium-doped diamonds were colorless or pale yellow-green with activation energies between 0.2 and 0.35 eV. Similar measurements by Wilson[14] in the temperature range 88 to 293°K on boron-doped synthetic diamonds yielded nearly 30 discrete activation energies ranging between 0.0029 and 0.087 eV. This was interpreted as evidence for impurity conduction or hopping transport which is commonly observed in heavily doped and highly compensated semiconductors at low temperatures.[15]

The present authors wish to report four-probe electrical conductivity measurements in the temperature range 223 to 323°K on a series of aluminum-doped and nominally boron-doped synthetic semiconducting diamonds. These measurements support the interpretation of the optical data which indicates that the same acceptor center, namely aluminum, is responsible for the semiconducting properties of both natural and synthetic semiconducting diamonds. The large range of activation energies derived from the electrical measurements is considered to be due to the progressive onset of impurity conduction at higher and higher temperatures with increasing concentrations of neutral (uncompensated) acceptor centers.

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EXPERIMENTAL

The aluminum-doped diamonds were pale steel-blue in color, similar to many natural semiconducting diamonds, with linear dimensions ~0.5 to 1.0 mm. The boron-doped specimens ranged in color between pale steel-blue and indigo with linear dimensions between 0.2 and 0.5 mm. Each specimen was mounted in a thin filament of Araldite expoxy resin on a fused silica plate. Four electrical pressure contacts, consisting of 4-mil-diam tungsten wires etched to a fine point, were arranged to be as nearly colinear as possible across the top surface of the diamond. The contacts were assembled in a jig under a microscope and the tungsten leads were finally cemented to the silica plate using Sauereisen No. 29 low-expansion ceramic cement. The specimen and contact assembly on the silica plate was placed inside a constant-temperature enclosure, in which the temperature could be controlled electronically to ±0.2°K in the temperature range 223 to 323°K.

All the contacts were non-Ohmic and partially rectifying, but far superior to similar contacts formed on natural diamond. This is presumably due to the large concentration of surface defects in the majority of synthetic diamonds as compared to that in natural specimens, producing a high-surface recombination velocity and inhibiting minority-carrier injection. Carefully designed electrical shielding virtually eliminated ac pickup, which can produce stray dc signals by rectification at the diamond contacts. Electrical contact noise was effectively eliminated by supplying the specimen current from a stabilized dc current supply working between 0.1 μA and 20 mA. Potentials and currents were measured by standard dc potentiometric methods. Temperatures were measured by a Chromel-Alumel thermocouple cemented to the silica plate as close to the diamond as possible. This was calibrated against a standard Nichrome/constantan thermocouple[16] to ±0.1°K.

RESULTS AND DISCUSSION

The electrical conductivity results for four nominally boron-doped synthetic diamonds (D1002 series), one aluminum-doped synthetic diamond (GECAL 1), and one natural type IIb diamond (CS2C), are compared in Fig. 1. For the synthetic diamonds, the absolute-resistivity values have probably only order of magnitude significance because of the irregular shape of these specimens and inhomogeneity in the distribution of acceptor centers. However, this does not affect the

[16] Supplied by the National Physical Laboratory, Teddington, England.

shapes of the curves, and the estimated precision of the measured resistance values and the temperature indicates that the slopes of the curves should be accurate to about $\pm 0.5\%$.

For a partially compensated p-type semiconductor with acceptor concentration $N_A > N_D$ the donor concentration, the number of holes in the valence band p, at a temperature T well below the exhaustion range, is given by

$$\frac{p(p+N_D)}{N_A-N_D-p}=\frac{2}{g}\frac{(2\pi m_h^* kT)^{3/2}}{h^2}\exp\left(\frac{-E_A}{kT}\right), \quad (1)$$

where E_A is the acceptor ionization energy and g the degeneracy parameter.[17] With an activation energy $E_A \sim 0.37$ eV, p will be neglible compared with N_A and N_D in the temperature range under consideration and Eq. (1) reduces to

$$p=\frac{2(N_A-N_D)}{gN_D}\left(\frac{2\pi m_h^* kT}{h^2}\right)^{3/2}\exp\left(\frac{-E_A}{kT}\right). \quad (2)$$

The resistivity ρ is given by $\rho=(pe\mu)^{-1}$, and if the mobility μ is considered to obey a power law with temperature such that $\mu=$ (constant) T^s, then

$$\ln\rho = (\text{constant}) - (\tfrac{3}{2}+s)\ln T + E_A/kT. \quad (3)$$

From Eq. (3), it can be seen that for $s=-\frac{3}{2}$, a plot of $\ln\rho$ versus T^{-1} will be a straight line with slope E_A/k, but for $s>-1.5$ the measured slope will yield a high value for E_A and for $s<-1.5$ a low value for E_A will be obtained.

The variation of Hall mobility as a function of temperature has been determined for a number of natural semiconducting diamonds.[1–3,5,6] Above ~ 373°K, the variation follows a T^s law, where s lies between -2.8 and -3.0. At lower temperatures the index s is somewhat specimen-dependent and changes continuously with temperature from ~ -0.7 at 223°K to -1.6 at 323°K. The graph of $\ln\rho$ versus T^{-1} for the natural diamond CS2C shown in Fig. 1 exhibits a very slight curvature and the mean slope gives a value for E_A, uncorrected for mobility variation, of 0.382 eV. No Hall-effect measurements have been made on this particular specimen, but applying a correction for the variation of mobility with temperature derived from measurements on another natural semiconducting diamond A100[7] this slope and curvature is consistent with a true value of $E_A = 0.373 \pm 0.003$ eV.

The aluminum-doped diamond GECAL 1 contains ~ 170 parts per million (ppm) aluminum, which is equivalent to $N_A \sim 3\times 10^{19}$ cm^{-3}. Infrared-absorption and recombination-radiation measurements on this specimen show that the neutral-acceptor concentration

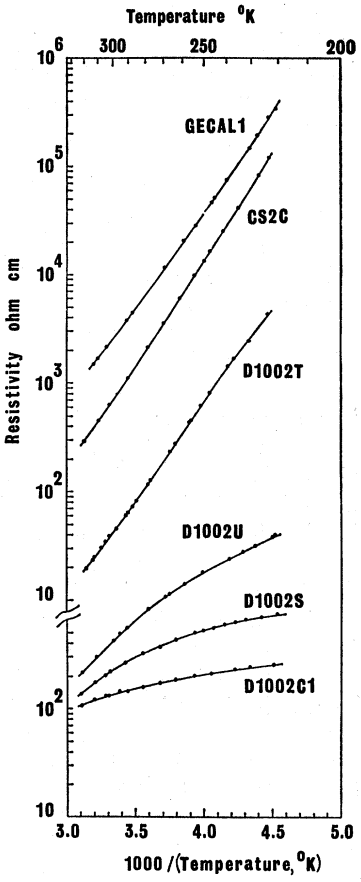

FIG. 1. Temperature dependence of the resistivity of a natural semiconducting diamond CS2C, an aluminum-doped synthetic diamond GECAL 1, and four boron-doped synthetic diamonds D1002. Absolute resistivity values have only order-of-magnitude significance because of the small size and irregular shape of the specimens and inhomogeneity in the distribution of acceptors. The actual shapes of the curves are, however, essentially correct. (Part of the ordinate axis has been repeated at the bottom of the figure to avoid intersecting curves.)

is about three times that observed in natural semiconducting diamonds, that is $\sim 10^{17}$ cm^{-3}, indicating $\sim 99.7\%$ compensation. The graph of $\ln\rho$ versus T^{-1} exhibits a slight curvature with increasing slope at lower temperatures, and the mean slope of the best straight line through the experimental points gives $E_A = 0.352$ eV. In the absence of any data concerning carrier mobilities in synthetic diamonds, it is probably reasonable to associate the lower value of E_A with the perturbing effect of the very high concentration of compensated acceptors.[18]

The nominally boron-doped diamond D1002T was selected from a batch of very pale blue specimens containing ~ 130 ppm aluminium. The infrared-absorption measurements indicate that the neutral-acceptor concentration is $\sim 3\times 10^{17}$ cm^{-3}. The mean slope of the high-temperature part of the curve gives a value for $E_A = 0.350$ eV, which is extremely close to the value obtained from GECAL 1, which has a very similar impurity concentration and compensation ratio. There is a change in slope to a slightly lower value at temperatures below 240°K. The nominally boron-doped diamonds D1002U, D1002S, and D1002C1, vary in color from pale blue to extremely dark blue. The depth of

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color is proportional to the strength of the photoionization continuum beginning at ~0.37 eV in the infrared and extending into the visible, and is, therefore, proportional to the neutral-acceptor concentration. The onset of impurity conduction at increasingly higher temperatures with increasing neutral-acceptor concentrations, is clearly seen in these specimens, and is just discernible below 240°K in D1002U.

Similar measurements on heavily doped p-type germanium have been reported by Fritzsche and Lark-Horovitz[19] and more recently by Davis and Compton.[20] At a constant acceptor-impurity concentration N_A of 2.5×10^{17} cm^{-3} in Ge, as the compensation ratio N_D/N_A decreases (neutral-acceptor concentration increases), impurity conduction sets in at increasingly higher temperatures. Since impurity conduction depends on phonon-induced hopping of carriers between adjacent neutral and ionized centers,[15] this conduction mechanism is critically dependent on the degree of overlap of the wave functions of the adjacent centers as well as on the compensation ratio. The acceptor ionization energy in diamond is ~30 times larger than in Ge, and the equivalent Bohr radius of the ground-state acceptor wave function is ~10 times smaller than for germanium. Hence the impurity-conduction mechanism would be expected to become important in diamond at much higher acceptor-impurity concentrations than for Ge, i.e. $\sim10^{19}$ cm^{-3} in diamond compared with $\sim10^{17}$ cm^{-3} in Ge.

The present electrical results, and extensive optical measurements down to ~50°K on the nominally boron-doped D1002-series synthetic diamonds, have failed to detect any features which can be definitely attributed to boron, even though chemical-impurity measurements on a complete charge of diamonds recovered from a pressure cell in a boron-doping experiment indicated extremely high boron concentrations >0.1%.[21] No measurements on individual diamonds by more sensitive techniques seem to have been made at the present time; the neutron-activation method cannot be used for boron. Since the boron atom is smaller and lighter than the aluminum atom, it would be expected to form an acceptor center with a lower ionization energy,[22] and, in the presence of a large concentration of donors, boron acceptors would be preferentially compensated, i.e., permanently ionized. One small additional feature has been observed in the recombination-radiation spectra from a very small number of the D1002 series diamonds at 55–70°K. This could possibly be associated with the decay of excitons bound to ionized boron acceptor centers.[7] Recombination-radiation measurements will shortly be extended to 4°K in order to investigate this feature in more detail. However, in view of the similarity between the electrical conduction measurements obtained from the nominally boron-doped diamond D1002T and the aluminum-doped diamond GECAL 1 (see Fig. 1), which from optical-absorption and impurity measurements are seen to contain similar concentrations of both neutral and compensated aluminum acceptors, it is difficult to believe that D1002T contains in addition >0.1% of compensated boron acceptors.

These conductivity measurements will shortly be extended to cover the full temperature range of interest 77 to 1200°K, and more recent batches of synthetic diamond will be investigated. ac Hall measurements are also planned which should give a more positive identification of the impurity-conduction mechanism, since the Hall field vanishes when the impurity-conduction mechanism becomes dominant.[15]

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One of us (A.T.C.) is grateful to the Science Research Council for the provision of a maintenance grant.

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[22] It has been brought to our notice that electrical conductivity measurements on natural diamonds, doped with boron by ion bombardment, indicate that boron produces an acceptor level with an ionization energy $E_A=0.25$ eV. Bombardment with lithium ions has produced n-type semiconducting diamond with a donor ionization energy of 0.29 eV. V. S. Vavilov, M. I. Guseva, E. A. Konorova, V. V. Krasnopevtsev, V. F. Sergienko, and V. V. Titov, Fiz. Tverd. Tela 8, 1964 (1966) [English transl.: Soviet Phys.—Solid State (to be published)].