Hall mobility and carrier concentration versus temperature for type Ila natural insulating diamond doped with boron by ion implantation

Paul R. de la Houssaye
Naval Ocean Systems Center, Code 553, 271 Catalina Boulevard, San Diego, California 92152-5000

Claude M. Penchina
University of Massachusetts, Department of Physics and Astronomy, Hadroncrrk Laboratory, Amherst, Massachusetts 01003

Charles A. Hewett
Naval Ocean Systems Center, Code 555, 271 Catalina Boulevard, San Diego, California 92152-5000

James R. Zeidler
Naval Ocean Systems Center, Code 804, 271 Catalina Boulevard, San Diego, California 92152-5000

Robert G. Wilson
Hughes Research Labs, 3011 Malibu Canyon Road, Malibu, California 90255

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A natural Ila diamond was implanted with boron ions at a substrate temperature of 80 K. Ohmic contacts (Mo/Au) were formed using a solid state reaction process. Van der Pauw resistivity/Hall measurements were taken as a function of temperature from room temperature to nearly 600 °C. Heating to approximately 350 °C was necessary to stabilize resistance values to over 3.4 MΩ/sq and 1.3 MΩ/sq for the unimplanted and implanted sides, respectively, indicating possible hydrogen incorporation into the diamond during annealing of the metallized sample in hydrogen. Comparison of the electrical properties of the implanted and unimplanted sides showed that the boron implant introduced electrically active acceptors.

INTRODUCTION

The unique properties of diamond relative to the semiconductors presently used to fabricate electronic devices (high electron and hole mobility, high saturation velocity, high energy band gap, and the highest thermal conductivity known), have focused attention upon its possible use in devices operating at high temperature or where radiation hardness is necessary. Ion implantation, a technique used extensively with other semiconductors to form layers of n- or p-type material at specific depths during different stages of processing, has yielded inconsistent results in diamond. These results are complicated by the tendency of the implantation to produce damaged layers, with electronic conduction similar to that of an n-type layer. Annealing of the sample after implantation does not remove this damage if the dose exceeds a critical value, while below this critical dose a significant fraction of the damage can be removed.

Studies on the effect of implantation in diamond have been further complicated by the wide variation in the electrical characteristics of natural diamond. Additionally, recent papers have questioned the role hydrogen plays in the resistivity of diamond, with large changes in the resistivity reported, downward by exposure of type Ia synthetic and type IIb natural diamonds to hydrogen plasma or upward by annealing in nitrogen after plasma chemical vapor deposition growth (with hydrogen) of thin films. Previous work has shown that adsorbed gases play a significant role in terminating dangling bonds on the diamond surface. Also, diamond has photoconductive properties which could introduce low level background currents. Nonetheless, many authors have attempted to draw conclusions based upon comparisons between two different diamond samples, one implanted, one not.

In this work we instead compare results from the front side with those from the back side of the same thin diamond slice, with only the front having been implanted. We are thus better able to observe the net change in the electrical transport due to the implant.

EXPERIMENT

Our starting material was a slice of natural type Ila diamond polished on both sides, 5×5 mm square, 0.25 mm thick. One side was successively implanted at a temperature of 80 K with boron ions at three different energies and respective doses: 25 keV (1.5×10¹⁴/cm²), 50 keV (2.1×10¹⁴/cm²), and 100 keV (3×10¹⁴/cm²). A Monte Carlo simulation for these implantation energies gave projected ranges of 512±139 Å, 993±218 Å, and 1871±311 Å, respectively. An experimental study, based on secondary-ion mass spectrometry (SIMS) measurements, of the depth distributions and range parameters for several elements (including boron) implanted into diamond can be found in Ref. 10, and indicates similar projected ranges. This combination of doses and energies was thus expected to produce a fairly uniform implanted layer about 0.2 μm thick, while not exceeding the critical dose for graphitization. After implantation, the sample was immediately re-
moved from the cold stage, transferred to a preheated furnace, and annealed in a dry nitrogen ambient at 990 °C for 10 min.

Next, the sample was thoroughly cleaned in a boiling, saturated solution of Cr₂O₃ in H₂SO₄ at about 160 °C for 10 min, and rinsed in de-ionized water. This was followed by 10 min in a boiling 50/50 solution of NH₂OH·H₂O (30% stock solution) and a subsequent de-ionized water rinse. This sequence is believed to successfully remove any graphitized layer that might have formed during the implant or anneal. It has also been shown to remove metallization from the diamond. After a nitrogen blow dry, the sample was loaded into a holder for ohmic contact metallization. A stainless-steel shadow mask with four small symmetric holes near the four corners of the sample was used to ensure the proper van der Pauw geometry. This assembly was then loaded into a UHV chamber and brought to vacuum (base pressure 8×10⁻⁹ Torr). A Mo (100 Å)/Au (1500 Å) layer was then deposited by electron beam evaporation. After removal from the system, the sample was placed in a furnace and annealed for 6 min at 960 °C in hydrogen. Further details on the characteristics of the ohmic contacts formed in this way can be found in Moazed et al.¹¹

For the first experiment, ohmic contacts were formed on the unimplanted side of the diamond. The sample was then placed in a standard ceramic (alumina) 24 pin chip carrier (nonmagnetic plating base) with all but the outer 4 leads removed, sandwiched between a sapphire wafer on the bottom (to prevent contact with the metal on the chip carrier ground plane) and a small piece of sapphire in the center of the top side (to prevent contact with a tungsten spring clip used to hold the whole assembly to the chip carrier). Both the chip carrier and the sapphire pieces were degreased separately by successive 10 min immersions in boiling trichloroethylene, cold acetone, and boiling methanol. Additionally, the sapphire pieces were immersed for 1:1:25 NH₄OH:H₂O₂:H₂O. The four contact pads on the diamond were then wire bonded to the appropriate contacts on the carrier and placed in the high-temperature van der Pauw resistivity/Hall effect measurement apparatus which is diagrammed in Fig. 1.

A few remarks should be made about the difficulties experienced in the design and operation of such a system. Avoiding reactions between extraneous gases and the diamond surface was of paramount importance. At high temperature, in the presence of oxygen or water vapor, diamond will be transformed to the graphitic phase of carbon. Also, as mentioned earlier, there is some question as to the electrical role of gases adsorbed into the bulk or on the surface. Thus, care was taken to ensure that the diamond was exposed to no other gas other than high-purity argon when at high temperature. A flow of ½ l/min of ultrahigh-purity argon was generated and fed into the system by passing argon through a purifier consisting of a quartz chamber filled with hot titanium chips. Stainless-steel tubing was used between the purifier and the quartz chamber; this tubing was baked under argon flow just prior to ramping up the diamond temperature. Two check valves and two sections of very small diameter stainless-steel tubing were used to prevent air from getting back into the system through the gas exit port, as well as to create a slight positive pressure in the system. In between the check valves, a hygrometer sensor was placed to measure the moisture content of the system, as a confirmation that there were no large system leaks (the dew point of the Argon was less than −115 °C). Additionally, the system was leak checked under pressure, just prior to the experiment.

With four ohmic contacts placed symmetrically on the corners of the sample, the resistivity was measured using the standard van der Pauw technique. This involves passing current through two adjacent contacts, measuring the voltage generated across the other two, and subsequent commutation of the contact pairs.¹² Homogeneity (uniformity of current flow) of the sample can be gauged by the form factor $f < 1.00$, which is a function of the difference in resistivity obtained when the current is passed through a second pair of contacts at 90° to the previous measurement.¹³ Ideally, for a homogeneous square sample with perfect point ohmic contacts, $f$ is equal to 1.00; the deviation from $f = 1.00$ can be used as a gauge of the sample inhomogeneity, or, if a homogeneous square sample is assumed, the data's self-consistency and/or the quality of the ohmic contacts. The Hall coefficient is determined by measuring voltages generated in diagonally opposed contacts when current is passed between the other two under the influence of a perpendicular magnetic field. The Hall coefficient yields the carrier concentration, and in conjunction with the resistivity, gives the carrier mobility. Again, the self-consistency of the results can be determined by switching sets of contacts and comparing the Hall voltages generated.

After the system was completely purged of air and the system integrity verified, the system was ramped very slowly to the desired temperature. At intervals of 15 to 20 min, a complete resistivity/Hall effect measurement was performed at either two or three different currents (4, 10, and in some cases 100 μA), and, for the Hall effect, at each
of three different magnetic fields (approx. 1800, 5200, and 8600 G). (Measurements at 100 μA were not attempted at the lower temperatures, where the sample resistance approached 1 MΩ and the current source its compliance limit of 100 V.)

After the measurement was complete, the diamond was removed from the chip carrier. The diamond sample and the sapphire pieces were cleaned as before, removing all prior contact metallization. Ohmic contacts were then fabricated on the implanted side, and identical resistivity/Hall effect measurements were performed as a function of temperature.

The experimental procedure for ramping the temperature (by ramping the heater current) and waiting for the temperature to stabilize was kept the same for both sets of measurements (of the unimplanted and implanted sides). This was done to ensure reproducibility of the actual sample temperature, given that one can be reasonably certain of an unknown temperature gradient between the sample and the thermocouple, not in direct thermal contact with the sample, located on the back side of the chip carrier (see Fig. 1).

RESULTS AND DISCUSSION

The initial room-temperature resistivities of the diamond sample in the argon ambient were unusually low, ranging from 62 kΩ/sq for the unimplanted side to 140 kΩ/sq for the implanted side, seemingly the reverse of what one might expect if the only difference in the sides was the implant. These resistances increased rapidly as a function of time when the sample was heated to a temperature of about 220 °C and stabilized at a value of about 1.2 MΩ/sq for the implanted side and about 1.4 MΩ/sq for the unimplanted side after about an hour. Further heating to 350 °C produced a much more stable value of 3.4 MΩ/sq for the unimplanted side, and 1.3 MΩ/sq for the implanted side (at 350 °C). One possible explanation is that the hydrogen introduced in the contact annealing step began to diffuse out of the diamond, and that the effects of the implant on the resistivity only became measurable after this hydrogen had diffused out of the diamond. Note that a similar effect has been seen in type Ia and IIb natural diamonds exposed to an energetic hydrogen plasma.5,6,14

After stabilization, the temperature of the diamond was reduced. Data were then taken as a function of temperature as the temperature was slowly ramped up to nearly 600 °C. A minimum of 20 min was allowed after changes in the heater current before the next measurement. In contrast to the data taken prior to stabilization, these data did not change appreciably with time after the thermocouple reading stabilized. Simultaneously, the self-consistency of the data, as represented by the form factors, improved substantially. The only Hall effect and resistivity data considered in evaluating the effect of the implanted boron ions are those obtained after stabilization. Additionally, resistivity measurements were required to give a form factor of greater than 0.95, and Hall data was required to conform to the American Society for Testing and Materials (ASTM) standard that measured Hall voltages differ by less than 10%.13

Figure 2 compares the resistivities of the two sides as a function of inverse temperature. It should be noted that, especially at the higher temperatures, the measured values for the unimplanted side will begin to approach those observed for the implanted side due to parallel conduction through the thin diamond sample to the implanted layer. The observed resistivity is thus much lower than would be expected in an unimplanted sample. Other authors have attempted to determine a carrier activation energy from a semi-log plot of the resistance versus inverse temperature.2,5 However, the resistance includes separate contributions from both the carrier concentration and the carrier mobility. Since the temperature dependence of the mobility can be significant,4,16-19 we analyze the carrier concentration directly.

For extrinsic material with holes as the dominant carrier type, the hole concentration (p) depends on the acceptor binding energy (EA) and temperature (T) as follows:20

$$\frac{p (p + N_D)}{N_A - N_D - p} = \frac{2}{h^2} \left( \frac{2\pi m^* kT}{h^2} \right)^{3/2} g_p e^{- (E_A/kT)}$$  \hspace{1cm} (1)

where gp is the “spin degeneracy” of holes on acceptors.21 The carrier concentration expressed by Eq. (1) may fall into one of three limiting regions. At a temperature low enough that p < N_D (and with p < N_A - N_D), this reduces to (region 1):

$$p = \frac{N_A - N_D}{N_D} 2 \left( \frac{2\pi m^* kT}{h^2} \right)^{3/2} g_p e^{- (E_A/kT)}$$  \hspace{1cm} (2)

and the slope of ln(pT⁻³/²) vs 1/kT should yield the carrier binding energy (or more accurately, the ionization enthalpy22-24). The temperature range over which p < N_D applies increases with the level of compensation (N_D/N_A). If the material is virtually uncompensated, the applicable temperature range of the above equation will be very small.

![FIG. 2. Comparison between the implanted and unimplanted side resistivities vs temperature after stabilization has occurred.](image-url)
FIG. 3. Log of the free sheet carrier concentration vs inverse temperature for the implanted side.

At higher $T$, where $p < N_A - N_D$ but $p > N_D$, the general case reduces to (region 2)

$$p = (N_A)^{1/2} \left( \frac{2\pi m^* kT}{h^2} \right)^{(3/4)} e^{-\left( \frac{E_A}{2kT} \right)}$$

(3)

and the slope of $\ln(pT^{3/4})$ vs $1/kT$ should yield half the acceptor binding energy (ionization enthalpy). At still higher $T$ (region 3), we get saturation and $p \approx N_A - N_D$. In this region the activation energy decreases to nearly zero. Thus one must be very careful when assigning an acceptor binding energy based solely on activation energy from a plot of this form. The result obtained can be off by as much as a factor of two or more depending on the assumptions made.

Figure 3 shows the log of the sheet carrier (hole) concentration plotted against the inverse temperature for the implanted side. Hall voltages showed consistently $p$-type behavior of the implanted side. The slope of $\ln(pT^{3/4})$ versus $1/kT$ obtained in the 600–850 K region corresponds to an energy of 0.29±0.04 eV, which in recent work has occasionally been (incorrectly) equated with the acceptor binding energy. Depending on which of the first two regions above applies, these same data actually imply an acceptor binding energy of between 0.18 and 0.49 eV. This is in agreement with Vavilov et al., who also observed a boron ionization energy of 0.19 eV, under the assumption that region 1 [Eq. (2)] applies. Below 600 K the temperature independent hole concentration implies a nearly constant background of holes from another acceptor level in the diamond (presumably region 3 for this level). This background should be subtracted out before a slope is determined, but due to the uncertainties in the baseline value, was not attempted here. Another possibility is the onset of another conduction mechanism, such as hopping. More data at higher temperatures are required to reduce the uncertainties described above. The key point, however, is unaltered: ion implantation has introduced a $p$-type dopant in diamond.

FIG. 4. Measured mobility as a function of inverse temperature for the implanted side.

Plotted in Fig. 4 is the measured mobility as a function of inverse temperature for the implanted side. Mobilities of between 30 and 60 cm$^2$/V s were observed, with a peak at about 350 °C. Similar mobility curves have been observed by other authors.

In order to verify system integrity, similar measurements were performed on a natural IIb (boron-doped) diamond. The slope of the measured free hole concentration, $p$, versus inverse temperature yielded an energy of about 0.33 eV, in agreement with previous measurements. The mobility of 400 cm$^2$/V s at 300 K was lower than that reported by Collins for natural diamond, but within the range reported for synthetic diamond by others.

The corresponding measured mobilities for the unimplanted backside are scattered widely around 3–5 cm$^2$/V s, occasionally reach negative values, and in almost all cases do not meet the ASTM standards. Shown in Fig. 5 are those that are within a factor of two of the ASTM standard; only 4 of these at the low-temperature end fall within the standard. The nonuniform, high resistivity in the sample (perhaps due to residual incorporated hydrogen in the

FIG. 5. Measured mobility as a function of inverse temperature for the unimplanted side.
sample), made the measurements unreliable by ASTM standards. The values of $p$, determined directly from Hall potentials that are for the most part near the sensitivity limit of the equipment, also show a large amount of scatter. This would be expected if there was a very small net carrier concentration on the backside.

CONCLUSIONS

Electrical transport measurements of the front and back sides of a slice of natural IIa diamond 0.25 mm thick, the front side of which was implanted with boron ions at a substrate temperature of 80 K, were utilized to determine the effect of the implant. The implant resulted in a $p$-type sheet carrier concentration of order $10^{11}/\text{cm}^2$ with a mobility of $\approx 50 \text{ cm}^2/\text{V s}$ at a temperature of 400 °C.

Prior to the measurements, the diamond was preheated to a temperature of over 300 °C for nearly an hour in a purified Ar ambient. During this time the resistivity of the diamond increased by nearly two orders of magnitude, eventually stabilizing with respect to time. The implanted side of the sample stabilized at a lower resistivity than the unimplanted side, further indicating a contribution to the conductivity due to the implant.

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