

## Doping Diamond for Electronic Application

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Diamond based electronic devices promise to exhibit unique properties. In order to realize devices diamond has to be doped to render it electrically conductive. In the present work the doping of diamond and of polycrystalline CVD diamond films are reviewed with particular emphasis to ion-implantation doping and to attempts to dope diamond by in-diffusion of the dopants. The quest for finding ways to obtain n-type conductivity in diamond will be critically examined.

**Key words :** Diamond, Doping, CVD, Ion-implantation, EPR measurement

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### I. Introduction

Diamond exhibits unique physical and chemical properties due to the extremely strong bonding of the carbon atoms in their  $sp^3$  hybridization. When undoped, diamond is a very wide band-gap semiconductor which, for all practical purposes, can be considered to be an insulator at room temperature. However, if doped, diamond can be rendered conductive, while maintaining its unique physical and chemical properties. Hence the great interest in doping diamond, as it is the basis special electronic devices.

Most conventional doping techniques which are commonly used in the Si technology are not applicable to diamond due to its tight binding. Below we will survey the various doping techniques and critically review their applicability to diamond.

Whereas p-type doping of diamond is well under control by the use of many techniques, hence opening up the possibility of realizing a large number of diamond based devices, the situation regarding n-type doping is more complicated. Tremendous efforts are devoted these days to finding suitable donor dopants and devising ways of introducing them into diamond. These will be briefly described below.

### II. General Considerations

Impurity atoms can, in principle, be introduced into diamond by a variety of methods many of which have, for the case of boron, yielded useful p-type conduction.<sup>1)</sup> Boron containing diamonds exist in nature (type IIb) and have also been produced in the laboratory under high pressure and high temperature (HPHT) conditions, in accord with the C phase diagram. This growth method, however, does not allow good device applications. Furthermore, it seems as if not all desired impurities can be introduced by this technique into the diamond matrix to serve as dopants. Doping diamond during HPHT syn-

thesis will thus not be further discussed here.

Impurities can, in general, be introduced into a solid by diffusion, either from the gas phase, from a surface coating or from an ion-implanted region. However, the extremely short bonding of the C atoms in diamond makes this thermodynamic process very difficult, if not impossible<sup>2)</sup> as will be described below.

Much work has been devoted to the growth of doped diamond layers by the CVD methods. Both p-type and potential n-type dopants (B and P, N, Li, Na.. respectively) have been introduced into the CVD reactors sometimes yielding diamond films which, according to SIMS evaluation, did contain the desired dopants<sup>3)</sup> and sometimes did show some dopant related electrical conduction. Whereas the case of p-type doping due to B is well under control, the situation regarding donor related conductivity is still unclear. Doping during CVD diamond growth has recently been reviewed by Okano *et. al.*<sup>4)</sup> and by others, so it will not be further discussed here.

Ion implantation, being a technique by which ions are forced into the target material, allows the introduction of any desired impurity into diamond, regardless of solubility or thermodynamic equilibrium conditions.<sup>5)</sup> It may thus be a particularly promising technique for doping diamond, provided that methods of annealing the damage that always accompanies the implantation process are found. These must remove the damage, drive the implants onto electrically active sites while avoiding graphitization. Recent results on doping diamond both p- and n-type by this method will be described below.

Finally, some novel approaches to doping diamond by either "forced diffusion" or by "neutron transmutation" will be critically examined.

A note of caution: It is important to bear in mind the unique properties of diamond and of CVD diamond films which can lead to erroneous interpretations of doping attempts. The fact that the stable bonding configuration of C is the graphitic  $sp^2$  hybridization, which yields con-

ductive centers, can lead to an electrical conductivity which is not related to real chemical doping but is rather due to broken graphitized bonds in the diamond bulk, or to graphite layers decorating grain boundaries in polycrystalline material. Accumulation of dopants along grain boundaries in CVD diamond films may lead to apparent dopant "incorporation", as apparent in SIMS, and to electrical conductivity along impurity decorated defects which have nothing to do with real chemical doping of diamond. Hence, most reliable doping results are those obtained for homoepitaxial diamond doped during CVD growth, or for single crystal diamonds implanted with dopants and as a control, identically implanted with inert ions

### III. p-Type Doping

Semiconducting, B containing, p-type diamonds exist in nature and have been synthesized both by HPHT and by CVD techniques. Good doping efficiencies and carrier mobilities, close to those found in the best natural type IIb diamonds, have been obtained.

Doping diamond by ion-implantation has also been accomplished, as previously reviewed by Kalish<sup>6)</sup> and by Prins.<sup>7)</sup> The accepted technique for implanting and annealing diamond is to implant B to low doses (below the graphitization limit<sup>8)</sup>) into cold diamond followed by in situ rapid annealing (the CIRA process ref. 9) and followed by further ex situ high temperature annealing. This procedure has recently yielded good electrical activation of the dopants, good hole mobilities and a very low compensation ratio, as described in detail in ref. 10 and as shown in Fig. 1.

An alternative way of obtaining thin heavily doped p-type layers in diamond is to utilize the fact that once a

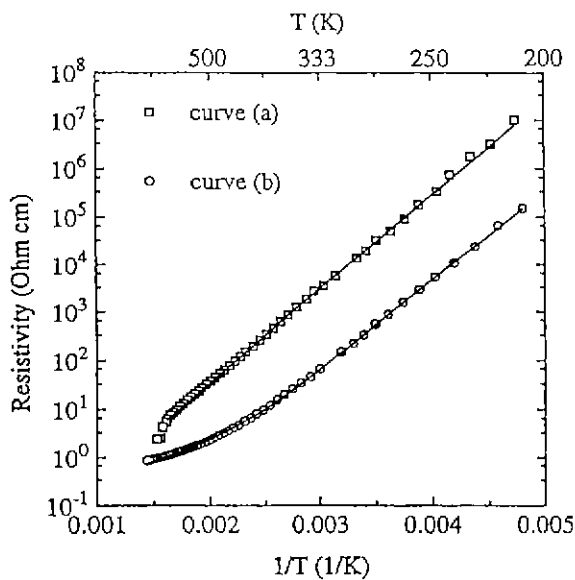


Fig. 1. Resistivity vs. 1/T for B doped diamond following 1050°C 10 min RTA (curve (a)) and 1450°C 10 min. (curve (b)).

critical damage level due to B ion-implantation has been reached, the damaged diamond will graphitize upon annealing.<sup>9)</sup> This graphitic layer can be removed by chemical etching, leaving the B implants in the tail of the ion distribution residing in an annealed diamond surface layer. This technique has been employed long ago by Braunstein and Kalish<sup>11)</sup> and more recently by Kalish *et al.*<sup>12)</sup> to yield highly conductive p-type layers in diamond and in CVD diamond films as required for the realization of good ohmic contacts to p-type diamond.

By performing consecutive low dose boron CIRA implantations followed by high temperature annealing it is possible to obtain any desired B doping level, i.e. doped layers with any desired conductivity and activation energy,<sup>13)</sup> as shown in Fig. 2.

Ion-implantation at elevated temperatures has been shown to inhibit amorphization and hence no graphite forms during annealing. Most recently, the Technion

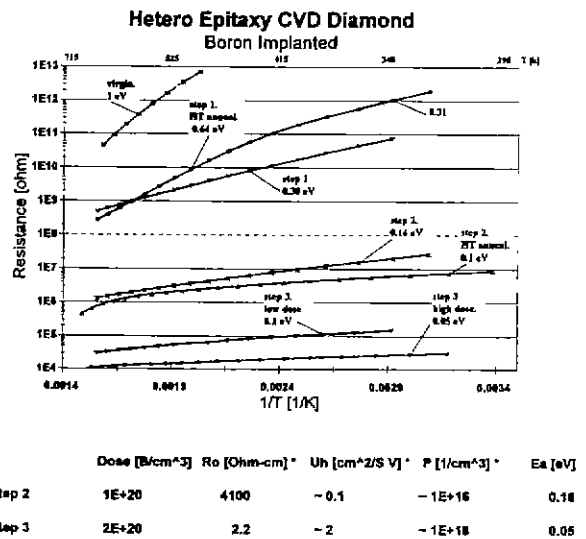


Fig. 2. Resistance vs. 1/T for B implanted CVD diamond at various consecutive doses.

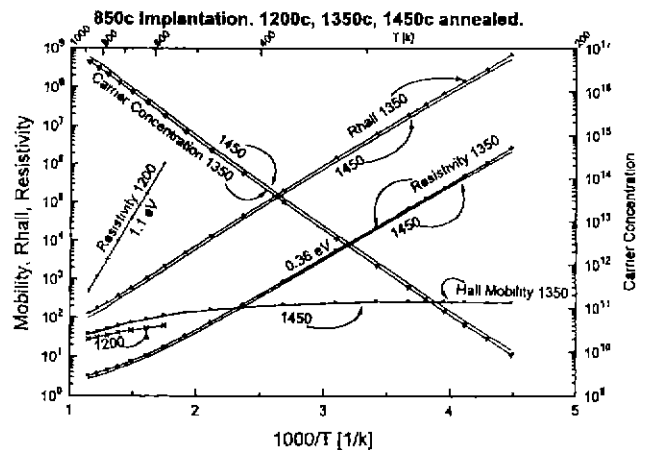


Fig. 3. Hall mobility and carrier concentration for not B implanted diamond following different annealing procedures.

group has performed B implantations into hot (800°C) type IIa diamond.<sup>13)</sup> Interestingly, immediately following the implantation, the sample exhibited a very high resistivity, however, annealing at high temperatures (1200, 1350 and 1450°C) has eventually reduced the resistivity, revealing clear B related conduction, with the well known B acceptor activation energy of 0.37 eV and a Hall mobility of  $\sim 200 \text{ cm}^2/\text{Vsec}$ . The results of this, yet unpublished work (13) are shown in Fig. 3.

#### IV. n-Type Doping

Effective n-type doping of diamond is, so far, inconclusive. There is as yet no clear indication what impurity atom may form a shallow enough donor level in diamond, nor is it known how to make good ohmic contact to an n-type diamond. Nevertheless, the great importance of the topic stimulates most intensive research, resulting in much progress.

##### 1. Phosphorus

Pioneering work of Okano and coworkers<sup>14)</sup> indicates that a donor state located about 0.1-0.2 eV below the conduction band of diamond can be found in P containing CVD diamond. By growing a diamond layered structure of p-type (by HF CVD growth with  $\text{B}_2\text{O}_3$ ) and n-type (by growth with  $\text{P}_2\text{O}_5$ ) Okano *et al.*<sup>15)</sup> could realize a diamond based p-n junction with distinct rectifying features, as shown in Fig. 4.

Recently a P doped single crystal diamond layer has been grown homoepitaxially by the microwave CVD technique. This layer which is obviously free of grain boundaries, has exhibited clear n-type features in Hall measurements with a RT mobility of about  $30 \text{ cm}^2/\text{Vs}$  (ref. 16).

Attempts to dope diamond with P by ion-implantation have so far yielded inconclusive results. Whereas Prins<sup>17)</sup> has observed some P related conduction in extremely low dose implanted diamond, intensive work of the Technion group could as yet not reproduce this result.

A novel approach to annealing diamond by laser irradiation of a deeply P implanted layer in diamond<sup>18)</sup> as

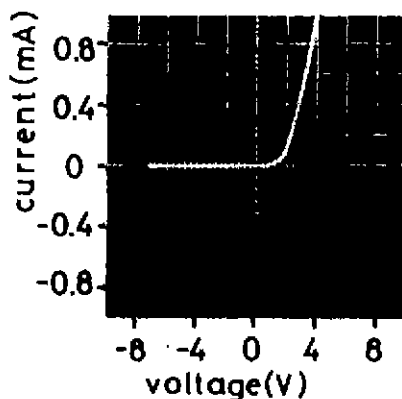


Fig. 4. I-V of CVD p(B)-n(P) junction at 300C.

shown that the implantation damage can be annealed by this method and about 50% of the P atoms reside on substitutional sites in the diamond lattice.<sup>19)</sup> However no conclusive electrical conductivity related to the P implants could be measured in such treated samples so far.

##### 2. Lithium and Sodium

Calculations by Kajihara *et al.*<sup>20)</sup> have suggested that group I elements (Li and Na) may, when occupying interstitial sites in the diamond lattice, act as shallow donors. More recent calculations<sup>21)</sup> indicate that substitutional Li will act as an acceptor in diamond.

The introduction of Li into diamond during CVD growth has not been published as yet, to the best of our knowledge.

The situation regarding diffusion of Li into diamond is unclear. Whereas recent publications<sup>22,23)</sup> report on SIMS observation of Li diffusing into diamond and into polycrystalline diamond films, intensive work at the Technion<sup>24)</sup> could not detect, by careful SIMS, any real penetration of Li into a single crystal diamond. This work could, however, indicate possible pitfalls in SIMS analysis of Li which may give rise to profiles which may look like diffusion related.

In the light of the above, it seems as if ion-implantation may be the method of choice for introduction of Li (and Na) into diamond. The lattice sites of Li in diamond following various implantation and annealing procedures have been determined by the use of the channeling technique.<sup>25,26)</sup> These show that about 40% of the Li occupy interstitial sites, where they are expected to act as donors, 20% reside on substitutional sites, where they may be acceptors, and the remaining 40% are in 'random' locations in the diamond crystal.

The electrical characterization of Li doped diamond relies on R(T) measurements, on thermopower measurements<sup>27)</sup> on electric field effects on the "forced" diffusion of Li<sup>28)</sup> and on some rectifying features found in Li implanted ptype diamonds.<sup>28)</sup> No conclusive Hall effect measurements have as yet been reported. Nevertheless,

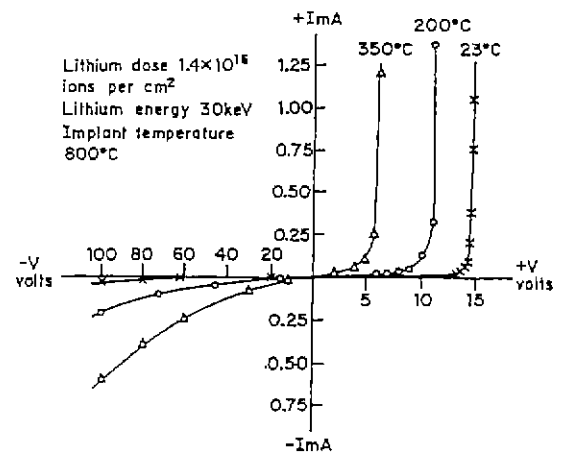


Fig. 5. I-V of p(type I Ib)-n(Li impl.) diamond.

the picture that emerges is that Li implanted into diamond can be electrically activated. Most recent results by Job *et al.*<sup>29)</sup> show that n-type conduction can be identified in Li implanted diamond and that higher conductivities are obtained following hot implantations. It seems as if high temperature annealing of Li implanted diamond does not necessarily improve the electrical activation of implanted Li, perhaps due to the capture of defects by Li and its passivation. Despite this fact, the Harwell group<sup>28)</sup> did succeed to obtain rectifying features in a p-type (IIb) diamond doped with Li by hot implantation (see Fig. 5).

### 3. Nitrogen

Nitrogen is a deep (1.7 eV) donor in diamond which can thus not affect, at room temperature, its electrical conductivity. Nevertheless, the possibility of using n-type (N doped) diamond for electron emitting devices makes controlled doping of diamond and CVD diamond films of great relevance. For this reason has the Technion group<sup>30)</sup> employed the know-how gained in B implantation doping of diamond to implantation dope diamond with N. The implanted diamond has been subjected to EPR measurements, which yield quantitative information on the amount of N occupying substitutional sites in an undamaged diamond environment, and to luminescence measurements which reveal N related complexes in the crystal. The results of this work show that about 50% of the implanted N occupy substitutional sites in the diamond lattice and that defect complexes similar to those found in natural N containing (type Ib) diamonds are formed by the implantation/annealing scheme that has been proven to yield good results for B implants in diamond.

## V. Novel Doping Approaches

Popovici and coworkers<sup>31)</sup> have proposed an interesting method for obtaining Li in diamond. It relies on a neutron induced nuclear reaction which transforms the  $^{10}\text{B}$  isotope to  $^7\text{Li}$ . Diamond films grown with  $^{10}\text{B}$  as a dopant were exposed to intensive neutron irradiation. The thus heavily damaged diamond has been subjected to thermal annealing which has partially restored the diamond structure, as verified by Raman and luminescence spectroscopies. A reduction in activation energy of the electrical conductivity in the sample has been attributed in ref. 31 to a possible compensation of the B with a donor level due to the formation of electrically active Li. However, such a compensation may well also be due to unannealed residual damage.

Whereas this transmutation doping approach may be of academic interest, it is unlikely to be a useful method for obtaining n-type diamond. The reasons being the very high damage level which accompanies the n irradiation and the high recoil of the  $^7\text{Li}$  following nuclear

alpha decay as well as the high background p-type conduction caused by the non transformed B in the diamond.

## VI. Conclusion

Tremendous advancement has taken place in the last decade in the realization of B doped diamond and in its use in a wide variety of applications. These include uses as chemically inert electrodes for electrochemistry, simple diamond based high temperature sensors and MIS logic devices. This advancement gives much hope that the search for n-type diamond will also soon yield useful results. Indeed the prospects of finding solutions to this problem are high in the light of the most recent results which indicate that P and perhaps Li may be useful donors in diamond. The very intensive research efforts in this topic will, hopefully soon yield results which will enable us to realize bipolar as well as cold cathode devices in diamond.

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