Physics – Uspekhi **37** (4) 407 – 411 (1994)

INSTRUMENTS AND METHODS OF INVESTIGATION PACS numbers: 61.72.Ww; 68.55.Ln

Possibilities and limitations of ion implantation in diamond, and comparison with other doping methods

V S Vavilov

Contents

Abstract. Diamond is a crystal with extremely strong atomic bonds. It is characterised by very low equilibrium parameters of the solubility and diffusion coefficients of impurities. Ion implantation therefore represents a natural alternative doping method. The published experimental results show that p-type and p^+-type layers can be formed by boron ion implantation. Implantation of Li^+ and C^+ produces n-type layers. Diamond films grown in the presence of phosphorus and sodium can also be electrically conducting. The efficiency of this method of introducing electrically active centres varies strongly with the temperature of diamond during implantation and with the conditions during the subsequent annealing.

1. 'Shallow' acceptors and donors in diamond

In very few cases the natural processes of growth of diamond have led to the formation of boron-doped semiconductor crystals. It follows that there is a way for direct imitation of nature. The properties of natural and synthetic diamonds containing boron have been described [1 – 3]. Judging by the available data, doping of synthetic diamond single crystals during growth with impurities that can have fairly shallow donor levels has not yet yielded the results comparable with the donor doping of Ge and Si crystals. The method of simultaneous prolonged application of high pressures and temperatures is complex and costly [1]. Moreover, the technologies used currently to grow diamonds at high temperatures and pressures result in an inhomogeneous distribution of boron atoms in a crystal. An attractive alternative of growing semiconductor diamond films from a gaseous plasma, containing hydrocarbon dissociation products, is now being rapidly developed [4].

The existing theoretical models described by Bernholc et al. [5] are in agreement with the experimental data on the effects of boron atoms replacing carbon and acting as acceptors with a fairly shallow energy level (E_v + 0.37 eV). It follows from these models that it would be desirable to continue the search for nonequilibrium methods that can be used to introduce impurities with shallow donor levels. These impurities include Li, Na, and P.

Growth of diamond films from a plasma [4, 6] and ion implantation are typical nonequilibrium processes. It is these two methods, developing in parallel, that should become the foundation for extensive use of diamonds in technology. Table 1 provides basic information about the expected and also the experimentally detected impurity centres with shallow energy levels in diamond.

2. Radiation damage and phase transitions

Some of the experimental investigations of ion implantation in diamond have been carried out at very high energies — up to 50 MeV [7], but the majority of the published results have been obtained under more usual conditions (40 – 350 keV). The range of unchannelled ions agrees quite well with calculations [8]. There are published data on the channelling, studied both to check the theory of the process and to determine the microstructure of impurity centres and defects; the latter aspect will be considered later. The parameters in the expression for the minimum yields of backscattered particles from diamond are very different from the corresponding parameters of silicon and germanium: the ratio u_1/a, where u_1 is the average amplitude of the lattice vibrations and a is the Thomas – Fermi screening radius, is 0.17 for diamond, but it is close to unity for Ge and Si. Data on the channelling of protons in carefully selected highest quality natural diamond crystals have been reported by Derry et al. [9]. The temperature dependence of this yield on the distance between the atomic chains in a channel are in agreement with the theory [10]. In the nearest future we can also

V S Vavilov P N Lebedev Physics Institute, Russian Academy of Sciences, Leninski prospekt 53, 117924 Moscow Tel. (095) 135 05 51

Received 24 November 1993
Uspekhi Fizicheskikh Nauk **164** (4) 429 – 433 (1994)
Translated by A Tybulewicz

Table 1. Shallow-level centres in diamond (atoms of N replacing C have deep donor levels).

	Acceptors		Donors			
Theory	Ref. [5]	Ref. [5]	Ref. [5]		Ref. [5]	
Impurity	Boron (replacing C)	Lithium (at interstices)	Sodium (at interstices)	Carbon (in complexes)	Substitutional phosphorus	Antimony
Energy level, eV	0.37	0.1 ± 10%			0.09—0.03	
Activation energy	0.37—0.09	0.1 eV				
Efficiency of doping by implanation	> 10%	≃1%			Low	Low
Efficiency of doping during growth of diamond films	> 10%					
Remarks	Boron is acceptor in natural semiconductor diamonds	Substitutional Li inactive? See Table 2		Disappears after annealing at > 800 °C	Low solubility	

Table 2.

Energy of Li^+ ions/keV	Dose/ ions cm^{-2}	Mobility/cm^2 V^{-1} s^{-1}	Surface density/cm^{-2}	Surface conductivity/Ω^{-1}
110	4.0×10^{15}	870 ± 10%	5.2×10^{10}	7.3×10^{-6}
310	3.0×10^{15}	650	2.4×10^{10}	2.6×10^{-6}
350	3.0×10^{15}	1070	2.3×10^{10}	4.0×10^{-6}
110	2.5×10^{16}	1030	2.3×10^{10}	3.8×10^{-6}

expect data on the channelling in large synthetic diamonds, which will be very interesting in relation to the task of determining the quality of their crystal lattice. We cannot exclude the possibility that the channelling in diamond may have some practical applications, in view of the data obtained for Si and GaAs [11, 12].

Very important and only partly understood topics are related to the nature of the spatial distribution and stability of radiation defects, which appear unavoidably in diamond as a result of ion implantation. The method for identification of such defects has been described in several monographs [1, 2, 7] and is still being developed. Many researchers have been justifiably cautious and even pessi-mistic about ion implantation doping of diamond because of the existence of other phases (graphite and amorphous carbon). The first experiments on the implantation of boron and other impurity ions [13] did not include the measurements of the Hall effect and the observed increase in the conductivity could not be interpreted unambigu-ously as the result of introduction of shallow acceptors. The conditions under which partial or complete recovery of the crystal lattice of diamond can take place have subsequently been identified for the implantation of boron [14]. References to earlier work can be found in the monograph by the present authors [2]. The ESR method used by Brosious et al. [15] has provided an independent confirmation that thermal (quasiequilibrium) annealing of ion-implanted diamond restores the crystal lattice. Later investigations carried out in the USA [16] have revealed regrowth of diamond films after their structure has been strongly disturbed by carbon ion implantation. It has been demonstrated earlier that the implantation of C^+ in diamond creates donor centres [17, 18]. The usual pro-longed annealing restores the lattice if the implantation dose (fluence) is less than 0.9×10^{14} cm^{-2} at 350 keV, but the degree (efficiency) of activation of the impurity centres is very low [19]. Above a critical dose of 1.5×10^{14} cm^{-2} 350-keV Sb^+ ions the accumulation of radiation damage results in graphitisation of diamond during subsequent annealing, as observed earlier also after implantation of other ions [2]. In some cases the effects of radiation damage have been minimised by implantation of ions in diamond heated to high temperatures [19—21]. This method can indeed avoid graphitisation and some of the implanted impurity atoms then occupy substitutional positions at the regular sites, but a parallel process is the generation of a large number of dislocations and possibly also of clusters of interstitial atoms as a result of the inter-action between point defects in the implanted layers [22]. Such defect clusters are very stable, they do not disappear even after annealing at 1450 °C, and they give rise to deep-level centres that compensate the effects of the implanted impurity, which is frequently typical of wide-gap crystals.

In 1988 Prins proposed [23] a qualitatively new method of double implantation of an electrically active impurity and carbon ions in diamond crystals kept at fairly low (liquid nitrogen) temperatures. Prins suggested that a subsequent brief high-temperature annealing immediately after implantation may result in a more effective activation of the impurity because of a high concentration of vacancies and interstitial atoms, which hardly diffuse at the implantation temperature. The effects of a brief annealing of ion-implanted diamond and the critical doses above which amorphous layers are formed were investigated by Prins by the method of the Rutherford backscattering and optical absorption measurements. The selected highest quality natural diamond crystals were implanted with C^+ ions in doses from 10^{15} to 3×10^{15} cm^{-2} along a direction excluding channelling and the ion energy was 200 keV. This was followed by two-minute annealing in a quartz furnace in a stream of argon at 1100 °C. Similar samples were subjected to conventional (isochronous) annealing in a vacuum furnace. The amorphisation dose was found to lie between 1.65×10^{15} and 3×10^{15} cm^{-2} for 200-keV C^+ ions at 77 K. At lower doses, both brief annealing at 1100 °C and isochronous annealing at 900 °C restored the structure. The results of annealing were however very different after larger doses. Isochronous annealing at 900 °C resulted in epitaxial growth, i.e. restoration of an almost perfect crystalline diamond under a graphitised layer at the

surface, whereas brief annealing produced a polycrystalline layer.

Prawer et al. [24] restored the structure of 'buried' radiation-damaged layers in natural diamond — the result of implantation of 2.8-MeV C^+ ions — by brief annealing with short (14 ns) laser radiation pulses. The range of these ions and its scatter were $R_p \pm \Delta R_p = 1.48 \pm 0.06$ μm. The laser radiation wavelength was 531 nm. It was estimated that the energy density in the disturbed layer of diamond was 200 J cm^{-2} per pulse. This value was considerably higher than the melting threshold of graphite (0.6 J cm^{-2} per pulse) or silicon (2 J cm^{-2} per pulse) [25, 26]. The thickness of the disordered layer was estimated to be about 200 nm. These estimates were deduced from the projected range of ions and its scatter, given by Ziegler et al. [27]. Implantation of C^+ ions took place in samples kept at about 77 K when — according to Prins et al. [28] — the resultant point radiation defects in diamond were practically immobile, which reduced the probability of formation of more complex defects that might be more difficult to anneal.

One of the unexpected results was that a dose of 10^{15} cm^{-2} of the C^+ ions, which at an energy of 90 keV amorphised the surface layer, did not result in amorphisation when the same C^+ ions penetrated much further. This indicated that the existence of a crystalline layer above a region where implanted ions are stopped reduces the disordering probability. According to the ideas of Prawer et al. [24], which are fully justified and date back to the well known work of Brinkman published in 1954 [29], each region at the end of the ion range can be regarded as representing briefly a very strongly excited volume of matter where the crystal structure is not retained and which cools in approximately 100 periods of the lattice vibrations (10^{-11} s). No estimates have yet been made of the probable pressure which the surrounding crystal exerts on such a region [29].

In the case of the results of Prawer et al. [24] it is worth noting particularly that if a laser is used in annealing, the range of energies deposited in the crystal and resulting in restoration of the lattice is only slightly below the threshold at which peeling of the whole diamond layer crossed by the implanted ions can take place (Prawer et al. used the term ablation). We can see from the results of the optical absorption and Rutherford backscattering measurements that annealing with single laser pulses results in only a partial restoration of the lattice. According to Prawer et al., repeated pulsed annealing should be more useful in future practice. A typical distribution of the implanted impurities and radiation defects has been reported by Zaitsev [7] many of whose experiments were carried out with ions of very high energies (up to 70 MeV). Zaitsev [7] has put forward the idea of fabrication of arrays of memory elements by irra-diation of diamond with single high-energy ions, by anal-ogy with the existing method used for sodium glasses [30].

3. Characteristics of doping during growth and of ion implantation in epitaxial and polycrystalline diamond films

The method of growing epitaxial diamond films on diamond substrates had been described by Aleksenko (Alexenko) and Spitsyn (Spitzyn) [6], who employed a plasma gas discharge in a static electric field. Other methods have been developed by American and Japanese authors [4]. Aleksenko and Spitsyn [6] reported that films grown from a plasma in the presence of boron contained this impurity and when the concentration of boron was less than 0.1%, its atoms were located primarily at the lattice sites. They were able to grow films with a very low resistivity (up to 10^{-3} Ω cm), but the carrier mobility did not exceed 15 cm^2 V^{-1} s^{-1}, which was approximately 100 times less than the mobility of holes in diamond single crystals of sufficiently good quality.

Some progress has also been made in the growth of diamond films containing donor impurities, particularly P and Sb. Judging by the results obtained in Moscow [6] and in Japan [31], the efficiency of formation of donor centres is low, i.e. the majority of antimony and phosphorus atoms remain neutral or their effects are compensated by simul-taneously formed deep-level capture centres (traps). This is in agreement with theoretical predictions [5].

The first report of ion implantation in epitaxial and poly-crystalline diamond films was presented at a recent seminar in Moscow [32]. Single-crystal epitaxial films were grown on oriented diamond substrates from a gaseous phase by the method of Spitsyn et al. [33]. Films grown on tungsten substrates were polycrystalline. Semiconductor films, con-tact regions, and structures for measurements of the Hall effect were prepared by the methods of photolithography and ion implantation. The energies of the ions and the implantation dose were calculated to ensure that the concentration of boron in the doped layer was 1.2×10^{20} cm^{-3}. The contact regions were formed by the implantation of boron in a dose of 5×10^{15} cm^{-2}. Annealing took place in a graphite container in $\approx 10^{-4}$ Pa vacuum. An investigation of the dependence of the con-ductivity of the doped films on the annealing temperature was in a qualitative agreement with the results of annealing of B^+-implanted natural and synthetic diamond crystals.

After annealing at temperatures up to 800 °C the conductivity of single-crystal and polycrystalline layers was found to be due to radiation defects, which disappeared at higher annealing temperatures [2, 23]. Electrical activation of boron began from 1300 °C. It was found that a further increase in the temperature of annealing of single-crystal films right up to 1600 °C increased the conductivity. The activation energy of conduction was about 0.1 eV and the hole mobility (deduced from the Hall effect) did not exceed 6 cm^{-2} V^{-1} s^{-1}. At higher temperatures the films fractured. Annealing of polycrystalline films at tempera-tures above 1300°C gave rise to a conducting layer over the whole surface, including the regions outside the doping zone, and this was evidently due to graphitisation. Therefore, polycrystalline films similar to those which were investigated cannot be subjected to high-temperature technologies.

4. Some aspects of practical applications of diamond in electronics and related technologies

A brief account will now be given of the currently available devices made of diamond and of the future trends. A comparison of the state of the art in 1992 with that in 1978, when the well-known book of Field (published in 1979) was

Table 3.

Applications or type of device	Type of diamond material essential in applications	Need for ion implantation	Remarks
Solid wear-resistant coatings	Polycrystalline diamond films or diamond-like carbon films	–	Applications are expanding fast
Heat sinks in microelectronics	Natural and synthetic diamonds; diamond films and ceramics	–	Already in use (only natural and synthetic diamond so far)
Transistors; diodes; integrated circuits	Natural diamond (physics); synthetic diamond; epitaxial films	+	First positive results
Particle detectors; dosimeters	Natural diamond; early applications of synthetic diamond and films	+	Stable operation (natural diamond)
Avalanche-transit diodes	Very homogeneous crystals needed	+	Likely to be available soon
Photoemitters (ultraviolet range)	Crystals and films can be used	+	"
Infrared photoresistors	"	+	"
Fast current switches	Natural diamond crystals are used		

still in press [1], shows that two varieties of diamond can be regarded as 'born again' after their appearance in the first edition of this book. These varieties are diamond films and ceramics [34]. Papers presented at the last two conferences on applications of diamond held in Moscow in 1991 and 1992 [35, 36] indicate that about ten teams are working in Russia and the Ukraine on the growth, characterisation, and practical applications of diamond films†. In my opinion the work of these teams and cost of maintaining such research, the scale of which in Western countries is incomparably greater [1, 4], are more than justified. The main technical applications investigated at present are not in the field of solid-state electronics, but in the production of wear-resistant, hard, transparent, and chemically stable coatings for machines and for applications in optics, including laser technology. The development of 'electronic' applications of diamond has been slower, but some devices are already used systematically. The first place among them is occupied by diamond heat sinks for which it is sufficient to use synthetic diamonds [37]. It is probable that films will soon be employed. Among devices that are used in biology and medicine it is worth mentioning particle counters and dosimeters constructed at the P M Lebedev Physics Institute in Moscow [38] in which the bulk polarisation is suppressed by injecting contacts which are formed by ion implantation (Table 3).

The progress in the construction of field-effect transistors [39] has been hindered primarily by the inhomogeneity of the available semiconductor diamonds. However, there is no doubt that, in principle, such transistors can be constructed.

Other existing and potential types of semiconductor diamond devices are described in my paper [40] and in a book by Vikulin and Stafeev [41].

I am grateful to A A Gippius, A M Zaitsev, V F Sergienko, B V Spitsyn, and R A Khmel'nitskii, as well as to J Prins (Johannesburg, South Africa) for their comments on ion implantation and physical phenomena in diamond.

†Unfortunately, there is no space here for reviewing the potential applications of diamond-like carbon films.

References

1. Field J (Ed.) *The Properties of Diamond* (New York: Academic Press, 1979) p. 677; *The Properties of Diamond and Diamond Films* (New York: Academic Press, 1992)
2. Vavilov V S, Gippius A A, Konorova E A *Elektronnye i Opticheskie Protsesy v Almaze* (Electronic and Optical Processes in Diamond) (Moscow: Nauka, 1985) p. 140
3. Bokii G B, et al. *Prirodnye i Sinteticheskie Almazy* (Natural and Synthetic Diamonds) (Moscow: Nauka, 1987) p. 255
4. *Abstracts of Papers presented at Materials Research Society (MRS) Meeting, Boston, MA, 1991, Symposia G and R* (Pittsburgh, MA: Materials Research Society, 1992)
5. Bernholc J, Kajihara S A, Antonelli A, in *Proceedings of Twentieth International Conference on Semiconductor Physics, Thessaloniki, 1990* Vol. 1 (Singapore: World Scientific, 1990) p 332
6. Alexenko A, Spitzyn B "Semiconductor diamonds made in USSR", in *Proceedings of 1991 International Diamond Conference, Nice, France*
7. Zaitsev A M, in *Almaz v Elektronnoi Tekhnike* (Diamond in Electronic Technology, Ed. V B Kvaskov) (Moscow: Energoatomizdat, 1990) p. 211
8. Burenkov A F, et al. *Tablitsa Parametrov Prostranstvennogo Raspredeleniya Ionnoimplantirovannykh Primesei* (Table of Parameters of Spatial Distribution of Ion-Implanted Impurities) (Minsk: Belarus' State University, 1980)
9. Derry T E, Fearick R W, Sellschop J P F *Phys. Rev. B* **24** 3675 (1981); **26** 17 (1982)
10. Barrett J H *Phys. Rev. B* **3** 1527 (1971)
11. Galkin G N, Dravin V A, Epifanov M S, et al. *Radiat. Eff.* **77** 57 (1983)
12. Laruelle F, Bagchi A, Tsuchiya M, et al. *Appl. Phys. Lett.* **56** 1561 (1990)
13. Vavilov V S, Guseva M I, Konorova E A, et al. *Fiz. Tverd. Tela (Leningrad)* **8** 1964 (1966) [*Sov. Phys. Solid State* **8** 1560 (1966)]
14. Vavilov V S, Guseva M I, Konorova E A, Sergienko V F *Fiz. Tekh. Poluprovodn.* **4** 17 (1970) [*Sov. Phys. Semicond.* **4** 12 (1970)]
15. Brosious P R, Corbett J W, Bourgoin J C *Phys. Status Solidi A* **21** 677 (1974)
16. Lin B, et al. *Nucl. Instrum. Methods Phys. Res. B* **45** 420 (1990)
17. Vavilov V S *Phys. Status Solidi A* **31** 11 (1975)
18. Braunstein G, Talmi A, Kalish R, et al. *Radiat. Eff.* **48** 139 (1980)
19. Braunstein G, Kalish R *Appl. Phys. Lett.* **38** 416 (1981)
20. Braunstein G, Kalish R *Nucl. Instrum. Methods* **209–210** 387 (1980)
21. Nelson R S, et al. British Patent No. 1 599 (7 October 1981)
22. Nelson R S, Hudson J A, Mazey D J, Piller R C *Proc. R. Soc. London Ser. A* **386** 211 (1983)
23. Prins J F *Phys. Rev. B* **38** 5576 (1988); *Mater. Sci. Rep.* **7** 271 (1992)

24. Prawer S, in *Proceedings of Materials Research Society (MRS) Meeting, Boston, MA, 1991* (Pittsburgh: Materials Research Society, 1992)
25. Venkatesan T, Jacobson D C, Gibson J M, et al. *Phys. Rev. Lett.* **53** 360 (1984)
26. Foti G *Radiat. Eff.* **48** 161 (1980)
27. Ziegler J, Biersack J P, Littmark U *The Stopping and Range of Ions in Solids* (Oxford: Pergamon, 1985)
28. Prins J F, Derry T E, Sellschop J P F *Nucl. Instrum. Methods Phys. Res. B* **18** 261 (1987)
29. Brinkman J A *J. Appl. Phys.* **25** 961 (1954)
30. Fischer B E, Spohr R *Proceedings of Workshop on Industrial Applications of Energy to Heavy Ions, Caen, France, 1989* p. 1
31. Okano K *Appl. Phys. A* **51** 344 (1990)
32. Denisenko A V, et al. "Electrophysical investigations of epitaxial diamond films doped with boron ions" in *1-i Mezhdunarodnyi Seminar 'Almaznye Plenki', Moskva, 1991* (Proceedings of First International Seminar on Diamond Films, Moscow, 1991) (Moscow—Ulan-Ude: Academy of Sciences of the USSR, 1991) p. 25
33. Spitsyn B V, in *Rost Kristallov* (Crystal Growth) (Moscow:Nauka, 1980) p. 55
34. Rotner Yu M, Rotner S M , in *Almaz v Elektronnoi Tekhnike* (Diamond in Electronic Technology, Ed. V B Kvaskov) (Moscow: Energoatomizdat, 1990) p. 186
35. *Perspektivy Primeneniya Almazov v Elektronike i Elektronnoi Tekhnike: Tezisy Dokladov Vsesoyuznoi Konferentsii, Moskwa, 1991* (Abstracts of Papers presented at All-Union Conference on Potential Applications of Diamonds in Electronics and Electronic Technology, Moscow, 1991) (Ed. V B Kvaskov) (Moscow, Energoatomizdat, 1991)
36. *Problemy Primeneniya Almaza v Elektronike: Tezisy Dokladov II Konferentsii, Moskwa, 1992* (Abstracts of Papers presented at Second Conference on Problems of Applications of Diamond in Electronics, Moscow, 1992) (Moscow: Znanie, 1992)
37. Novikov N V, Gontar' A G , in *Almaz v Elektronnoi Tekhnike* (Diamond in Electronic Technology, Ed. V B Kvaskov) (Moscow: Energoatomizdat, 1990) p. 57
38. Kozlov S F, Konorova E A "Method for fabrication of diamond detectors of nuclear radiations" USSR Patent No. 224 697 (1968); see also Konorova E A, Kozlov S F *Fiz. Tekh. Poluprovodn.* **4** 1865 (1970) [*Sov. Phys. Semicond.* **4** 1600 (1971)
39. Mel'nikov A A, Zaitsev A M, et al., in *Almaz v Elektronnoi Tekhnike* (Diamond in Electronic Technology, Ed. V B Kvaskov) (Moscow: Energoatomizdat, 1990) p. 228
40. Vavilov V S "Diamond as a material for solid-state electronics" (invited paper), in *Proceedings of Materials Research Society (MRS) Meeting, Boston, MA, 1991* (Pittsburgh: Materials Research Society, 1992)
41. Vikulin I M, Stafeev V I *Fizika Poluprovodnikovykh Priborov* (Physics of Semiconductor Devices) (Moscow: Radio i Svyaz' 1990)