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Ohmic Contacts to Semiconducting Diamond

FY 90 Annual Report

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ADMINISTRATIVE INFORMATION

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Released under authority of
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APPENDICES

FY 90 ANNUAL REPORT

METAL DEPOSITION SYSTEM IMPROVEMENTS

Early in FY 90, work was carried out to improve the electron beam evaporation system in order to achieve better deposited films. The basic system is a Perkin-Elmer ion-pumped vacuum chamber, with a three-hearth, single-gun e-beam evaporator. Four improvements were made to the system. The system was thoroughly cleaned and new ion pump elements, an e-gun beam adjust unit, and a more accurate crystal monitor were installed. The system now has a base pressure of 3 × 10^{-9} Torr, and can easily deposit high-melting-temperature metals such as Ta with an accurately controlled thickness. Improved shadow masks were also fabricated for better alignment and control of corner contacts for electrical transport measurements.

COMPARATIVE RESISTIVITY OF DIFFERENT METALLIZATIONS

Previously, we had investigated Mo, Mo/Au, and Mo/Ni/Au contacts to diamond. We have now investigated Ta/Au contacts and found qualitatively similar results. The annealed contacts are ohmic in response, with an electrical resistance that decreases sharply (10 orders of magnitude) as a function of annealing time at 950°C. The minimum values for room temperature resistance occur after approximately 30 minutes. Analysis using Auger electron spectroscopy, scanning electron microscopy, and x-ray diffraction established the presence of precipitates consisting of a carbide phase at the original tantalum-diamond interface. Preliminary results for Ti/Au and V/Au indicate similar behavior. (Details are contained in references 1-3.*)

CONTACT BONDABILITY AND ADHERANCE

A necessary property for ohmic contacts is the ability to form adherent wire bonds. To test the contacts for bondability, 10-mil gold wires were bonded to the contacts by using an ultrasonic ball bonder. Pull-to-failure test results indicated that wires typically fractured at a load of 4.2 grams, while the bonds to the contacts remained intact and attached to the diamond. (Diamond samples 5 × 5 × 0.25 mm^3 could be picked up by a single bonded wire.) See reference 2.

SPECIFIC CONTACT RESISTANCE MEASUREMENTS

One of the main achievements of the past year was the selection and implementation of a metallization pattern for analyzing the specific contact resistance of the ohmic contacts (reference 4). We have chosen to use the circular transmission line geometry and analysis first proposed by Reeves (*Solid State Electronics*, 1980, vol. 23, pp 487-490), consisting of two metallized rings concentric to a metal dot. This allows irregularly shaped samples to be analyzed. For accurate analysis, a thin conducting layer is required. We have applied this technique to four samples so far: two highly doped epitaxial films grown by Dr. Michael Geis of MIT Lincoln Labs, one naturally boron-doped semiconducting diamond 50 microns in thickness, and a similar naturally boron-doped semiconducting diamond 250 microns in thickness. Both naturally doped diamonds, as well as the substrates for epitaxial

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* Appendices A-F contain the text of articles referenced by number in this report.

growth were provided by Dr. Michael Seal of Drukker International, B. V. The specific contact resistances measured were in the range of 3×10^{-6} to 2×10^{-5} ohm-cm^2 for the highly doped films using Ti/Au contacts. The 50-micron diamond had a specific contact resistance of about 2×10^{-3} ohm-cm^2, while that of the similarly doped 250-micron-thick sample was about 2×10^{-2} ohm-cm^2, both with Mo/Au contacts. As expected, the contacts to the highly doped samples showed better specific contact resistances than the lightly doped samples. It is evident that the thickness of the conducting layer influences the measurement. These results indicate that the ohmic contacts to diamond should not be a limiting factor for device performance. Specific contact resistance measurements are expected to be completed in FY 91 for Mo and Ti, with comparisons being made to other metals, such as Pt. A comparison of sputter-deposited ohmic contacts prepared by Drukker International, B. V. with those deposited at NOSC is also under way.

ELECTRICAL TRANSPORT MEASUREMENT FACILITY

An electrical transport facility is being developed with Naval Ocean Systems Center (NOSC) Independent Research (IR) funds under project ZW16 administered by Dr. Alan Gordon. The use of this equipment to measure the carrier mobilities and sheet resistivities on ion-implanted boron is described in reference 5. The facility has also been used under this task for Hall Effect and Van der Pauw resistivity measurements on Li-doped films provided by Research Triangle Institute (RTI). Additionally, CVD diamond films prepared by Prof. Rod Dillon at the University of Nebraska will be characterized in FY 91.

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3. Moazad, K. L., J. R. Zeidler, and M. J. Taylor. 1990. "Metallization of Semiconducting Diamond: Mo, Mo/Au, and Mo/Ni/Au," in Diamond, Silicon Carbide and Related Wide Bandgap Semiconductors, J. T. Glass, R. Messier, and N. Fujimori, eds., *Mater. Res. Soc. Symp. Proc.*, vol. 162, pp. 347–353.

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5. De la Houssaye, P. R., C. Penchina, C. A. Hewett, R. G. Wilson, and J. R. Zeidler. 1991. "Electrical Activation of Boron Implanted into Diamond," to be published in the proceedings of the Second International Conference on the New Diamond Science and Technology.

APPENDIX A

A THERMALLY ACTIVATED SOLID STATE REACTION PROCESS FOR FABRICATING OHMIC CONTACTS TO SEMICONDUCTING DIAMOND

(Reference 1)

A thermally activated solid state reaction process for fabricating ohmic contacts to semiconducting diamond

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Techniques have been developed to produce ohmic contacts to naturally occurring boron doped semiconducting diamond. Thin films of Mo, Mo/Au, and Mo/Ni/Au deposited on diamond produced adherent ohmic contacts after annealing at 950 °C. A thermally activated solid state reaction which produces a refractory carbide precipitate at the original diamond/metal interface is the principal factor in affecting the properties of the contacts. The interface reaction has been characterized using Auger electron spectroscopy, scanning electron microscopy, x-ray diffraction, metallography, and *I-V* measurements.

I. INTRODUCTION

There is an ever increasing need for electronic devices that provide high power, or operate at extremely high frequency, and can also perform reliably in adverse operating environments.[1,2] Adverse operating environments of interest include exposure to high temperatures, to high levels of radiation, to corrosive media, or to some combination of these conditions. The requirement to cool existing electronic devices is a significant engineering problem in supersonic aircraft and space-based vehicles.[3] Other applications where the demand for these devices exists include motor vehicles, power generation, and well logging.[4]

Table I provides a list of the melting or dissociation temperatures, the theoretical intrinsic limits, and the band gap energies of various semiconductors. Note that while silicon and gallium arsenide do not melt until 1420 and 1238 °C, respectively, the corresponding theoretical intrinsic limit at which the material ceases to function as a semiconductor is 350 and 450 °C, respectively. Consequently, the silicon- and gallium arsenide-based devices require auxiliary cooling for operating temperatures exceeding 350 and 450 °C, respectively. The use of wide band gap semiconductors such as diamond, silicon carbide, and boron nitride could extend the operating temperature of devices to temperatures in excess of 1000 °C.

Recent advances in the epitaxial growth of silicon carbide, diamond, boron nitride, and other wide band gap semiconductors offer the potential for developing new types of device structures which can be utilized in applications where existing devices are ineffective.[1,4–7] These semiconductors, in addition to the capability of operating at higher temperatures, possess other unique physical, chemical, optical, and electronic properties that would be useful in many applications. For example, diamond windows were used for the infrared radiometers on the Pioneer spacecraft which operated within the hostile atmosphere of Venus.[8]

Semiconducting diamond is a promising material for high frequency and for high power device applications due to its high carrier saturation velocity, high breakdown voltage, relatively low dielectric constant, and high thermal conductivity. Comparative values of the Johnson's figure of merit[9] for high frequency and high power performance and the Keyes' figure of merit[10] for transistor switching speed for various semiconductors are provided by Davis *et al.*[1] Diamond is shown to have significant advantage over other semiconductors based on both the Johnson and the Keyes' figures of merit.[1] The unique physical, electronic, and optical properties of the wide band gap semiconductors also provide promise for new classes of high voltage optoelectronic switching devices.[11,12]

An important requirement for any emerging device technology is the development of suitable electrical contacts. The challenge is to produce electrical contacts which are compatible with the unique physical and chemical properties of diamond and are also capable of sustained operation in the severe operating conditions in which the devices are intended to operate. This paper will discuss techniques for the production of ohmic electrical contacts to semiconducting diamond which are compatible, as far as possible, with present microelectronics production methods and yet provide the desired performance characteristics.

TABLE I. Selected properties of semiconductors

Semiconductors	Band gap energy (eV)	Theoretical intrinsic limit (°C)	Melt temp. (°C)
Ge	0.71	100	937
Si	1.12	300–350	1420
GaAs	1.43	450	1238
GaP	2.24	800	1470
AlGaAs	1.43–2.15	375–475	···
AlGaP	2.24–2.45	550	···
SiC	2.3–2.9	800–1200	a
Diamond	5.5	1100	b
BN	7.5	···	3000

[a] Sublimes above 1800 °C.
[b] Transforms to graphite above 1200 °C.

II. BACKGROUND

It is rarely possible to achieve truly ohmic contacts with any semiconducting device. The contacts are generally regarded as satisfactory if the potential drop across the contact is small compared to that across the active portion of the device. Consequently, ohmic contacts are often formed by doping the semiconductor very heavily in the vicinity of the metal contact in order to reduce the width of the potential barrier at the metal/semiconductor interface. Although the barrier height is not affected appreciably by doping, the reduction in the barrier width results in an increased tunneling probability for electrons through the potential barrier. Another approach to obtaining ohmic contacts to semiconductors is to reduce the barrier height by appropriate matching of the metal work function to the band structure of the semiconductor. A third approach depends on recombination in the depletion region of surface defects induced by intentionally damaging the surface of the semiconductor. A detailed discussion of these methods and a summary of the diverse techniques utilized to produce ohmic contacts to semiconductors are noted elsewhere.[13]

Low resistance ohmic contacts to wide band gap semiconducting materials are expected to be difficult to form because of the large barrier height which results when a metal is deposited on the surface of the semiconductor. For example, evaporated gold films on boron doped semiconducting diamond were shown to provide a barrier height of 1.73 eV.[14] The situation is further complicated by the fact that diamond is a covalently bonded semiconductor with a high density of surface states leading to a barrier height essentially independent of the metal work function.[15,16] Further, it is difficult to produce a heavily doped surface layer in diamond. Nonetheless, ohmic contacts to semiconducting diamond have been produced by several distinctly different methods, as discussed below.

Previous attempts to develop ohmic contacts to natural and to synthetic diamond have been made in conjunction with measurements of the electrical transport, photoconductivity, and other physical properties of these materials. Ohmic contacts to natural and synthetic diamond have also been produced for prototype nuclear radiation detectors, high temperature thermistor elements, and light sensitive switches.

Metal contacts applied to smooth semiconducting diamond surfaces have exhibited an immeasurably large electrical impedance, due to the large potential barrier at the diamond/metal interface. When metal is placed in contact with a mechanically damaged area such as a crack, a corner, or an area which was deliberately roughened, reasonably good electrical conductivity has been obtained. Successful electrical transport[17,18] and infrared photoconductivity[19] measurements were made using colloidal graphite[11,17] or silver paint contacts[2,19,20] on roughened surfaces, or point contacts on the edge of a polished block.[18] The silver paint and colloidal graphite contacts are mechanically fragile and electrically noisy. The rough surface features and the large concentrations of surface defects of early synthetic semiconducting diamonds allowed electrical transport measurements to be made using point contacts.[21–24] These contacts were reported to be non-ohmic and partially rectifying, but far superior to similar contacts formed on natural diamond. Point contacts to type IIb diamond were evaluated as a function of the work function of the metal and were found to be rectifying contacts over the temperature range of 25–300 °C.[25] The metals investigated in this study were In, Al, Cu, W, Ag, and Pt.

The transition metals have an affinity for carbon, and as suggested by Seal,[26] transition metal/noble metal alloys in molten state will etch the surface of diamond by dissolving the surface, forming low resistivity carbide compounds, and enhancing the diffusion of the noble metal into the diamond.

Rogers and Raal[27] first used the approach suggested by Seal[26] to form thermistor elements from natural semiconducting diamond with a silver–copper–titanium alloy (63% Ag, 25% Cu, 12% Ti). Collins *et al.*[28] used gold–tantalum (99% Au, 1% Ta) and gold–tantalum–aluminum (90% Au, 9% Ta, 1% Al) alloys using electron beam welding to form electrical contacts to natural insulating and semiconducting diamond surfaces. The use of these *e*-beam welded contacts for ultraviolet photoconductivity measurements of both insulating and semiconducting diamond[28–31] resulted in an increase in signal to noise ratio of more than a factor of 10 over that obtained with silver paint contacts. None of these early investigations attempted to characterize the surface reactions which produced the ohmic behavior. In addition, no attempt was made to make comparative studies of these alloys.

Another method of producing ohmic contacts to diamond relies on the impingement of energetic ions into the diamond surface, e.g., sputtering, ion implantation, etc. Sputtered contacts of Ti/Pt/Au to natural diamond (type IIa) have been used as ohmic contacts in a study of high voltage optoelectronic switches.[11] In another study,[32] hard conducting diamond layers were produced by carbon implantation above a threshold dose of $\sim 3\times10^{16}\,\mathrm{cm}^{-2}$. More recently, it has been reported[33] that a graded structure of silicon/silicon carbide/diamond has been produced by "ion mixing" to reduce the barrier height and obtain ohmic contacts to diamond. In another study,[34] boron ions were implanted (35 keV, $3\times10^{16}\,\mathrm{cm}^{-2}$) into naturally boron-doped semiconducting diamond (type IIb) and fairly low resistance contacts could be obtained by just pressing metal probes against the contact areas.

Another method of applying electrical contacts to diamond[35] is to heat the diamond sample in an inert atmosphere to a temperature of 1500 °C. This treatment produces a layer of graphite on all exposed diamond surfaces. Affixing a wire to the graphite layer on the diamond was shown to produce ohmic contacts to diamond.[31] This approach has also been utilized as a method of applying large area metal contacts to both natural and synthetic semiconducting diamond.[28] The graphite layers can be selectively removed, without damage to the metal contacts, by boiling the diamond in a mixture of perchloric, sulfuric, and nitric acids. The production of a graphite surface layer by a laser beam has been proposed by Burgemeister.[36] More recently, an ArF laser was used to modify the surface of types IIa and IIb diamonds to a depth of 40–60 nm.[37] The laser modified layers were stable ohmic contacts to type IIb diamond up to 1800 °C.

Many of the methods described above are inadequate for producing durable ohmic contacts for diamond devices for the following reasons

(a) Dimensional integrity for metallization of contacts to diamond using a liquid phase process, such as electron-beam welding, is difficult to achieve.

(b) The liquid phase reaction process can not be accurately controlled to achieve reproducible results and to minimize contact resistance.

(c) The effect on the electrical properties of the contacts by formation of defects, or by formation of sp^2 (graphitic) bonds produced by techniques such as sputtering, ion implantation, or laser annealing, etc. has not been fully determined.

(d) Graphite layers produced by some forms of particle bombardment or thermal reactions are easily removed by various chemical treatments. Consequently, the long-term reliability of contacts produced by these techniques are questionable.

(e) It is difficult to produce durable wire bonds to the graphite layer. Therefore, the formation of mechanically stable contacts to graphitized diamond surfaces is impractical.

II. OHMIC CONTACTS USING A THERMALLY ACTIVATED SOLID STATE REACTION

The overall goal of this research is to develop procedures for fabrication of strongly adherent low-resistance ohmic contacts to diamond for microelectronics device applications. For the reasons cited above, the scope of this study, at the outset, was limited to electrical contacts produced by vapor deposition of metals which form stable carbides.

In an earlier communication,[38] it was demonstrated that evaporated and annealed films of Ta/Au and of Ti/Au produced ohmic electrical contacts to natural semiconducting diamond (⟨C⟩). The Ta/Au films deposited on ⟨C⟩ were annealed for 1 h at 885 °C. The Ti/Au films deposited on ⟨C⟩ were annealed for 1 h at 775 °C to prevent the allotropic transformation, at 880 °C, of alpha-titanium to beta-titanium. The Ta/Au and Ti/Au contacts to ⟨C⟩ were annealed in a quartz tube furnace in an atmosphere of flowing purified hydrogen gas. No significant change in the electrical response of the ⟨C⟩/Ta/Au or the ⟨C⟩/Ti/Au samples were observed when reannealed for an additional hour under the annealing conditions that were used initially. It was concluded that the reaction products had stabilized during the initial hour of annealing. In a recent paper,[2] ohmic contacts to epitaxial semiconducting diamond films were produced by electron beam evaporation of titanium onto a boron doped diamond epitaxial film held at a temperature of 400 °C. However, at this substrate temperature evaporated films of tungsten, molybdenum, and gold each formed a rectifying contact to boron-doped epitaxial diamond films.

None of the studies cited above investigated the diamond/metal interface or the role of the reaction at the interface on the electrical properties of the contacts. This paper will examine and characterize the thermally activated solid state reaction at the diamond/metal interface and its effect on the electrical properties of the contacts. Further, we will show that electron beam evaporated films of molybdenum, molybdenum/gold, and molybdenum/nickel/gold deposited on natural boron-doped semiconducting diamond, will all provide ohmic contacts after annealing the deposited films at 950 °C. It is further shown that there is an optimal annealing time at this temperature which produces a minimum contact resistance. This optimal annealing time is shown to be associated with the random nucleation and growth of carbide precipitates at the original diamond/metal interface. The relative adherence of the metals examined in this study will also be discussed.

IV. ADAPTATION OF PHOTOLITHOGRAPHIC TECHNIQUES FOR DIAMOND SUBSTRATES

Comparative measurements of the electrical resistance of the contacts were made using a series of rectangular pads 120 × 300 μm, each separated from the adjacent pad by systematically increasing distances of 5, 10, 20, 30, and 50 μm, as shown in Fig. 1.

The initial results using standard photolithographic techniques were found to be unsatisfactory for two principal reasons. First, the freshly deposited metal film did not adhere to the diamond surface and would be dislodged during the photoresist lift-off step. Second, the photoresist would deteriorate during the deposition of the metal film because of the excessive heat generated by the relatively high vaporization temperatures of the refractory metals utilized.

The approach that was utilized incorporated a silicon nitride film 0.15–0.2 μm thick grown on the cleaned diamond surface. Photoresist was spun onto the silicon nitride film, exposed through a photolithographic mask and developed to reveal the rectangles described above. The silicon nitride film below the rectangles is chemically etched off, thereby exposing the diamond surface for selective metalli-

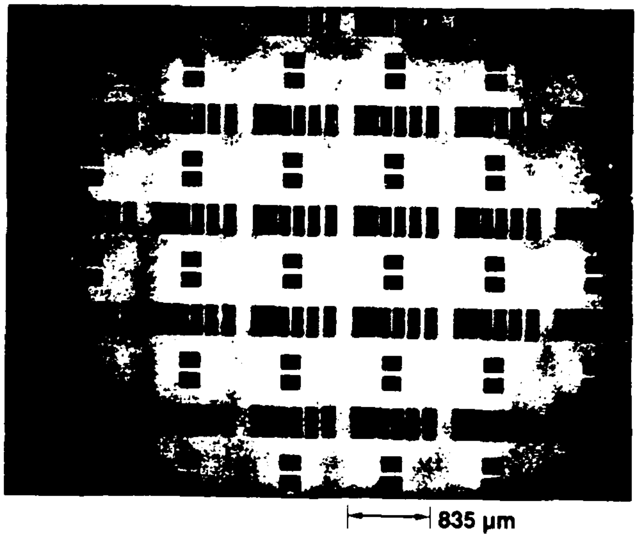

FIG. 1. Photograph of the Shockley photolithographic mask with rectangular pads 120 × 300 μm with spacings of 5, 10, 20, 30, and 50 μm in each series.

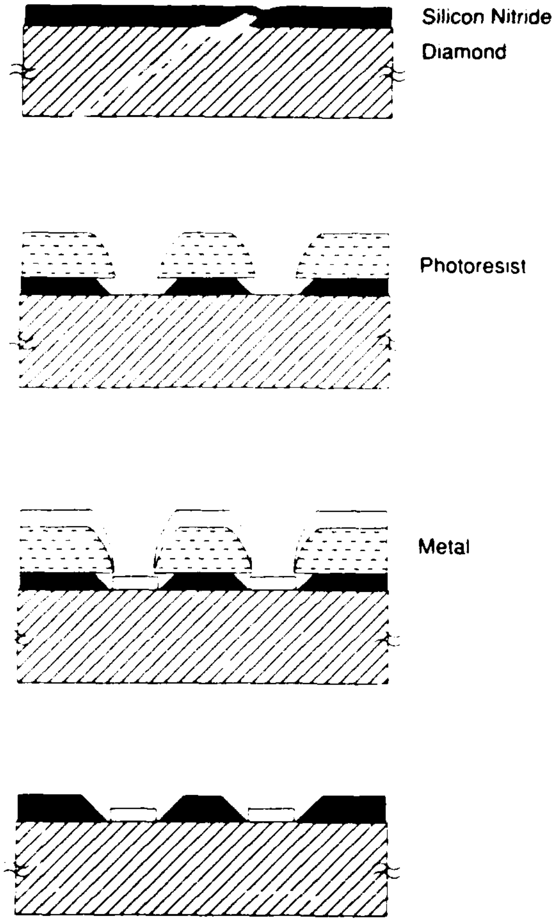

FIG. 2. Schematic of the processing sequence for metallizing diamond samples.

zation. A schematic diagram of the processing sequence is illustrated in Fig. 2.

The samples were next placed in an ion-pumped ultrahigh vacuum system that contains an electron beam heated source as well as a resistively heated source. The electron beam evaporation source was utilized for the refractory metals, while the resistively heated source is used for metallic components that vaporize effectively at temperatures below 2000 °C. With this system, it is possible to vaporize combinations of metals sequentially or simultaneously. Both abrupt and graded interfaces between two layer and three layer metal contacts have been produced in this system.

Following the deposition, the photoresist was chemically removed which also removes the metal from all but the rectangular pads. The configuration of the sample at this point consists of metallized rectangular pads on the surface of the diamond substrate separated by silicon nitride covered regions between the metallized pads. At this juncture, the sample was annealed.

The annealing step is an essential part of the process to produce ohmic contacts that will adhere to the diamond. Subsequent to annealing, the silicon nitride layer is removed by hydrofluoric acid. The sample now consists of metallized and annealed rectangular mesas separated from one another on the bare diamond surface.

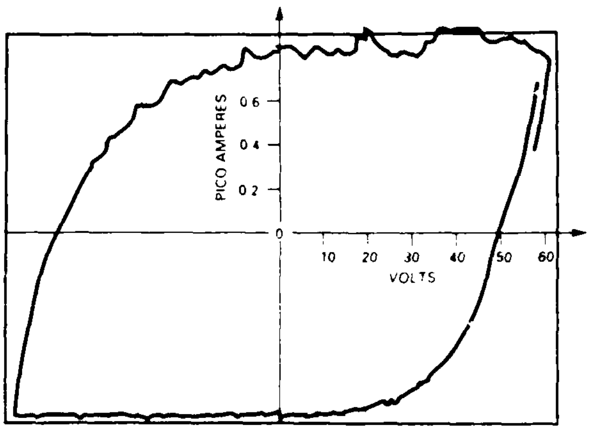

FIG. 3. Plot of current vs voltage for as-received diamond samples. The applied potential was ramped (saw tooth) ± 60 V dc.

V. ELECTRICAL MEASUREMENTS

The diamond samples that were used in this study were naturally occurring semiconducting grade (type IIb) which are *p* type due to the presence of boron at concentrations in the mid 10^{16} cm^{-3} and carrier concentrations in the mid 10^{14} cm^{-3}, as determined by secondary ion mass spectroscopy (SIMS) and Hall measurements, respectively. Electrical measurements were made using a curve tracer. A voltage was applied to each set of adjacent rectangular metallized pads and the *I-V* response was recorded. The electrical response of the as-received samples at applied potentials less than 100 V is shown in Fig. 3. A photograph of the metallized pads after metal deposition and prior to annealing is shown in Fig. 4. The electrical response of the samples after deposition but prior to annealing exhibited rectifying behavior of the same order of magnitude (a current of less than 1 pA at an applied potential of 10 V) as the as-received samples, illustrated in Fig. 5. Following the annealing step, a

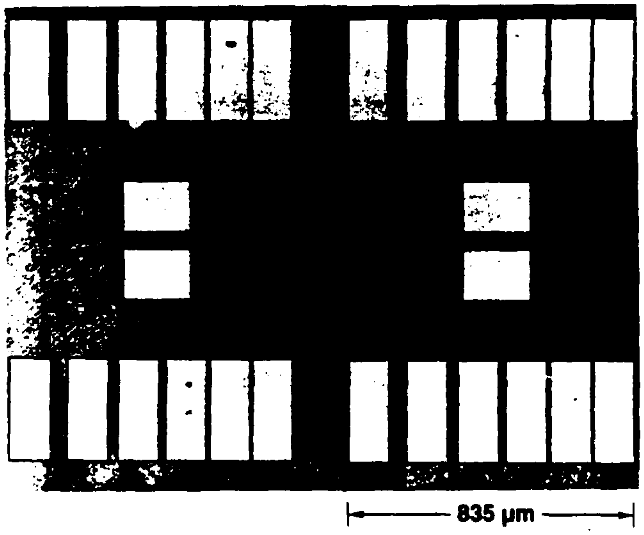

FIG. 4. Photograph of metal deposits in rectangular pads prior to annealing.

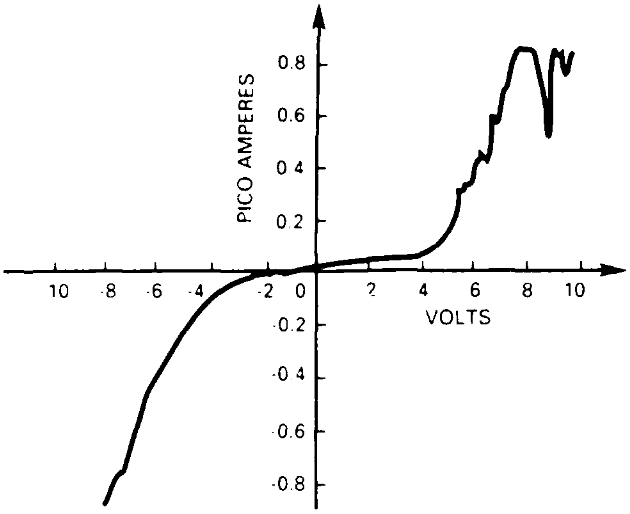

FIG. 5. Plot of current vs voltage for as-deposited metal contacts prior to annealing. The applied potential was ramped (saw tooth) ± 10 V dc.

current of 1 mA is produced at an applied potential of 2.5 V. As shown in Fig. 6, the response is clearly ohmic. These results are equivalent to those obtained with Ta/Au and with Ti/Au contacts to diamond.[18] Nickel films 15–25 nm thick deposited over molybdenum films 10–15 nm thick, after annealing at 950 °C, produced a tenaciously adherent ohmic contact. In fact, the annealed films could not be completely removed even by immersing the samples in a highly corrosive hot solution of chromic oxide in sulfuric acid. Usually, a gold film 150–500 nm thick was deposited over the reactive metal, i.e., Mo, Ta, Ti, etc., to prevent deterioration of the reactive metal film and to facilitate wire bonding to the contacts.

The effect of annealing time at 950 °C on the room temperature resistance of molybdenum films (~10–25 nm thick) contacted to diamond is shown in Fig. 7. It is quite clear that the contact resistance decreases continuously with increasing annealing time to ~8 min at this temperature. Annealing beyond 8 min, however, results in a slight increase in the contact resistance.

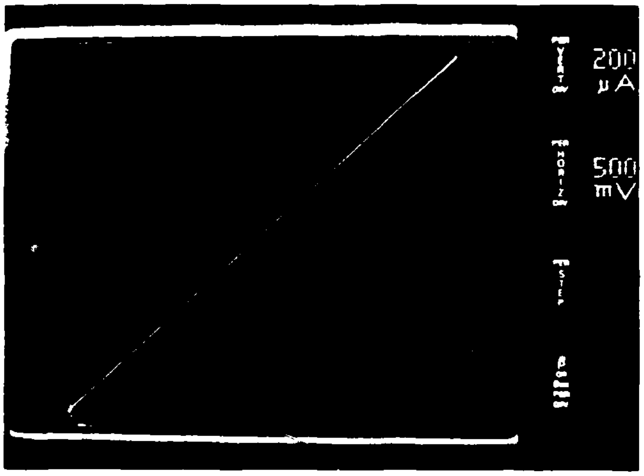

FIG. 6. Plot of current vs voltage for metallized contacts after annealing.

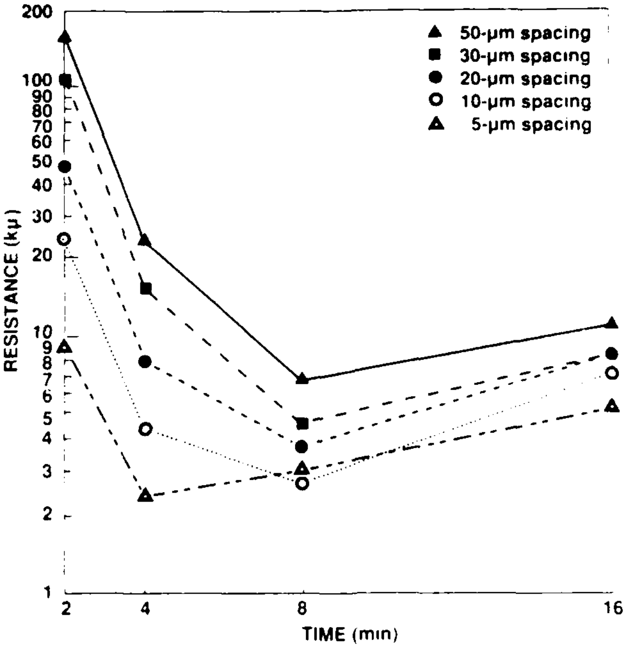

FIG. 7. Room temperature resistance as a function of annealing time at 950° C for (C)/Mo contacts various pad spacings.

Similar results were obtained for annealed samples of (C)/Mo/Ni/Au with deposited film thicknesses of 10–25 nm molybdenum, 15–50 nm nickel, 150–500 nm gold, as seen in Fig. 8. However, annealing of (C)/Mo/Ni/Au samples at 950 °C resulted in liquation of a Ni–Au alloy and partial segregation of the alloy into droplets without the loss of the dimensional integrity of the contacts laterally.

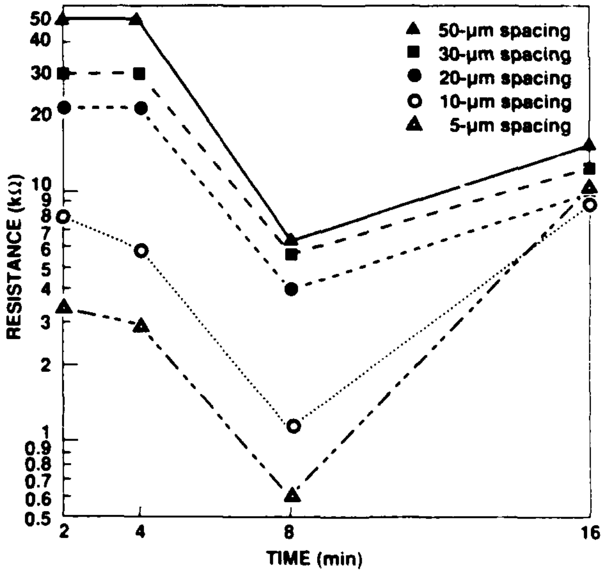

FIG. 8. Room temperature resistance as a function of annealing time at 950° C for (C)/Mo/Ni/Au contacts for various pad spacings.

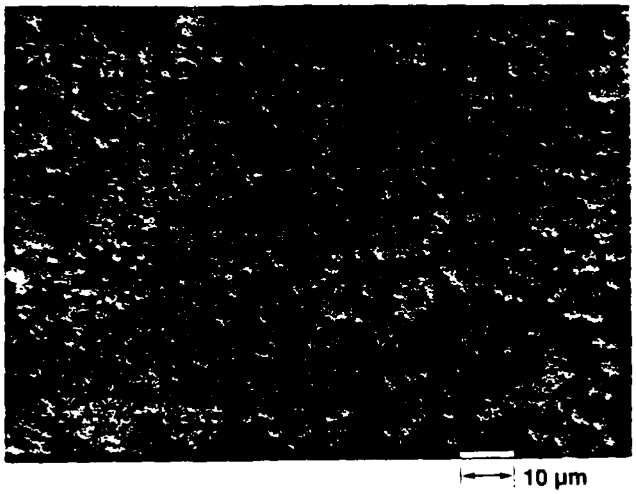

FIG. 9. SEM micrograph of a diamond sample that had been metallized with molybdenum, annealed at 950 °C for 8 min and etched. Random "patches" of carbide precipitates remain at the original diamond/metal interface.

VI. PROPERTIES OF THE DIAMOND/METAL INTERFACE

The removal of the metal films prior to annealing is easily accomplished. However, attempts to remove the metal films after annealing have been only partially successful, even after numerous cycles of prolonged immersion in hot solutions of chromic acid. As can be seen in Figs. 9 and 10, remnants of the reaction product of the refractory carbide forming metal with the diamond substrate persist even after several attempts to remove the deposit by etching.

Scanning electron microscopy (SEM) and metallographic studies of the annealed samples as a function of annealing time clearly substantiated that carbide precipitation progresses as a function of time at 950 °C. As illustrated in Fig. 9, isolated "patches" where carbide precipitation had occurred are separated from one another by regions devoid of carbide precipitates for a ⟨C⟩/Mo sample that was annealed for 8 min at 950 °C. Figure 10 illustrates the presence of a monolithic polycrystalline film of carbide for a ⟨C⟩/Mo sample that had been annealed for 16 min at 950 °C. These studies indicate that the minimum value in the resistance of the contacts is obtained prior to the formation of a monolithic carbide phase at the metal/diamond interface, as demonstrated in Figs. 9 and 10.

Auger electron spectroscopy (AES) depth profiling of the annealed samples clearly demonstrated that the carbon *KLL* Auger transition at the metal/diamond interface had the characteristics associated with carbon in a combined state and not that which is associated with adsorbed carbon or with diamond.[39,40] The AES spectrum obtained at the vacuum/metal interface and that which was obtained after depth profiling toward the original metal/diamond interface is shown in Fig. 11. X-ray diffraction studies, using copper *Kα* radiation, of the annealed ⟨C⟩/Mo and of ⟨C⟩/Mo/Au samples, with the gold film removed after annealing, produced a peak at $2\theta = 37.8°$ and a much weaker peak at $2\theta = 79.6°$. These diffraction peaks are due to {111} and {222} planes of Mo_2C, respectively. The absence of other

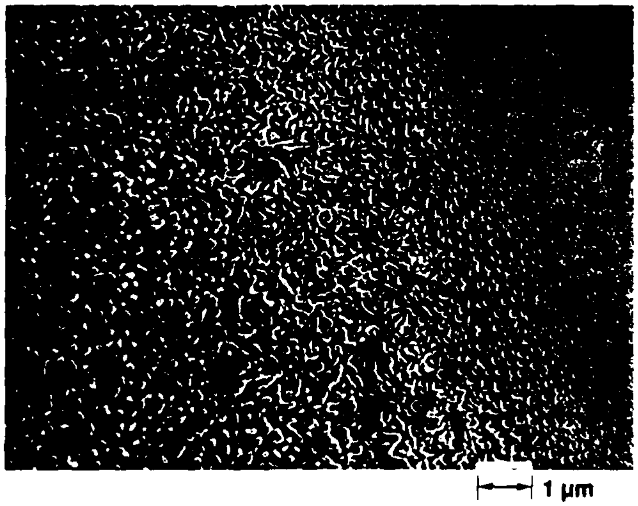

FIG. 10. SEM micrograph of a diamond sample that had been metallized with molybdenum, annealed at 950 °C for 16 min and etched. A monolithic polycrystalline carbide phase remains at the interface.

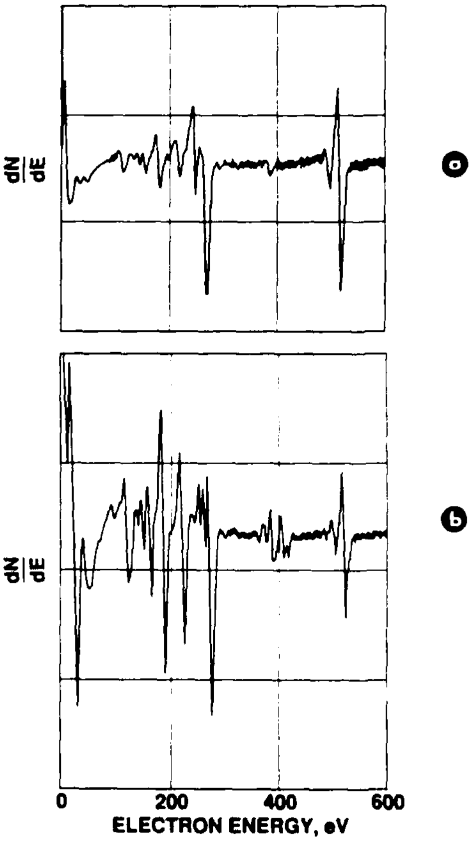

FIG. 11. Auger spectra of (a) the vacuum/molybdenum interface and of (b) the molybdenum/diamond interface. Note the considerable change in the carbon spectra (260–275 eV region) associated with the two interfaces.

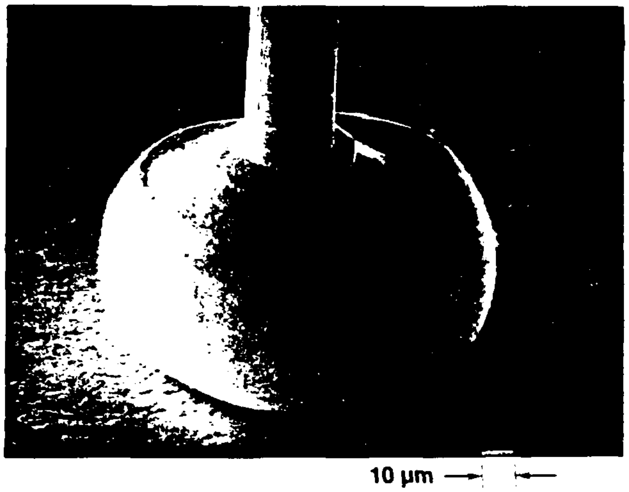

FIG. 12. SEM micrograph of gold wire bonded to a sample of ⟨C⟩/Mo/Au.

Mo_2C diffraction peaks (originating from {200}, {220}, and {311} planes) is likely due to a high degree of preferred orientation of the carbide phase in relation to the single crystalline diamond substrate. However, due to the extreme thinness of the carbide films, it is imprudent to completely rule out the possibility that the most intense peak may originate from the transition carbide phase $Mo_{0.42}C_{0.58}$.

VII. ADHERENCE OF METAL CONTACTS TO DIAMOND

The adherence of the metal contacts to diamond depends on the contact metal and the annealing conditions that were utilized. The best results, to date, were obtained with ⟨C⟩/Mo/Au and ⟨C⟩/Mo/Ni/Au samples annealed in a flowing purified hydrogen atmosphere at 950 °C for 6–8 min. The adherence of the metal contacts to diamond in these samples were sufficient to allow ball and wedge bonds to be made with gold wires using an ultrasonic wire bonder, as shown in Fig. 12. The relative adherence of molybdenum to diamond, of gold to molybdenum and of gold to diamond is illustrated in Fig. 13. This figure is an optical micrograph of a diamond sample that was annealed at 950 °C after a molybdenum film had been deposited on the diamond surface and a gold film had been deposited on the molybdenum film. Due to the geometry of the evaporation sources and because a shadow mask was used, there was a slight off-set of the gold film relative to the molybdenum film. Consequently, there were three distinct regions of deposited metal on the diamond substrate: identified as (a) Mo, (b) Au/Mo, and (c) Au. The lack of adherence of gold to diamond relative to that of gold to molybdenum to diamond and to molybdenum to diamond is clearly evident in Fig. 13.

Although the adherence of the annealed tantalum films to diamond was acceptable, the gold film deposits over the tantalum films had a tendency to delaminate during the lift-off of the photoresist, as shown in Fig. 14. The adherence of titanium/gold films to diamond after 1 h anneal at 775 °C was inferior to Mo, Mo/Au, and Mo/Ni/Au. Attempts to consistently produce adherent metal contacts to diamond using nickel were unsuccessful, as seen in Fig. 15. In a few instances where the nickel films adhered sufficiently to the semiconducting diamond substrate to enable *I–V* measurements, the contacts displayed ohmic response. The resistance measurements of a ⟨C⟩/Ni/Au sample, annealed at 900 °C for 1 h, were 760, 800, 1200, 1300, and 2000 Ω between adjacent contact pads separated by 5, 10, 20, 30, and 50 μm, respectively. Although, there is uncertainty regarding the thermodynamic stability of Ni_3C below 60 kbars,[41,42] there can be no disagreement regarding the superior stability of molybdenum carbide, tantalum carbide, or titanium carbide relative to nickel carbide.[43,44] Therefore, the relatively poor adherence of nickel to diamond compared to the adherence of molybdenum to diamond, etc. is not totally unexpected.

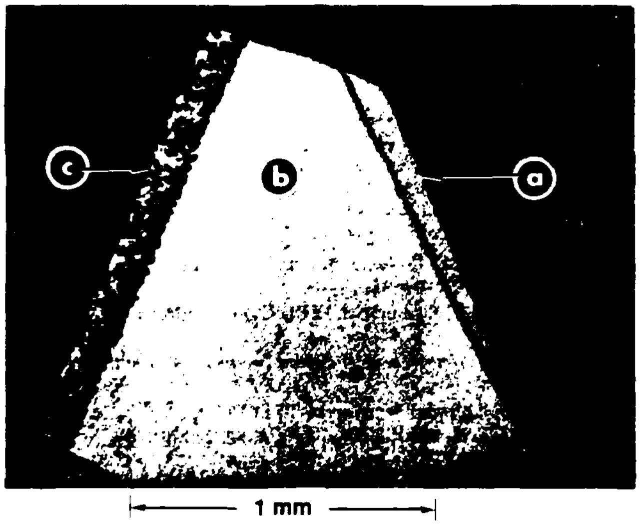

FIG. 13. Photograph of an annealed ⟨C⟩/Mo/Au sample depicting relatively good adherence of (a) Mo to ⟨C⟩, (b) Au to Mo to ⟨C⟩, and (c) relatively poor adherence of Au to ⟨C⟩.

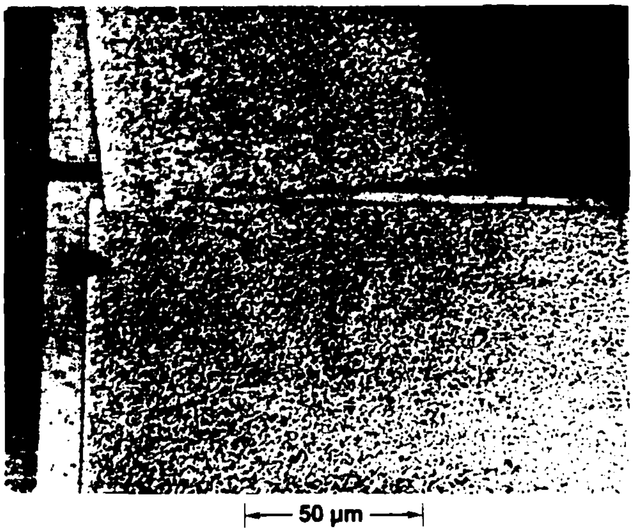

FIG. 14. Micrograph of a ⟨C⟩/Ta/Au sample illustrating delamination the gold film from the tantalum film during photoresist lift-off.

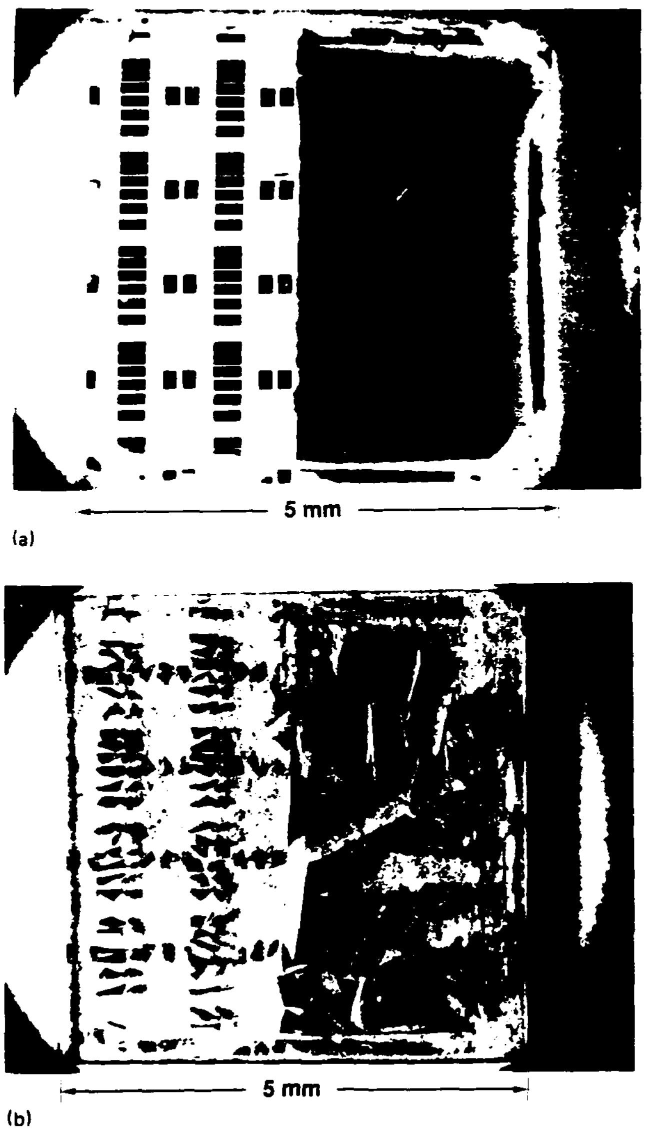

FIG. 15. Photograph of a ⟨C⟩/Ni sample; (a) prior to annealing and (b) subsequent to annealing, illustrating lack of adherence of Ni to ⟨C⟩.

VIII. CONCLUSIONS

Techniques have been developed to produce ohmic contacts to naturally occurring boron doped (p type) semiconducting diamond with very low carrier concentrations. The approach that was adopted is compatible with manufacturing practices that are used in the production of other microelectronic devices.

It was shown that electron-beam deposition of thin films of Mo, Mo/Au, and Mo/Ni/Au on naturally boron-doped semiconducting diamond produced ohmic contacts subsequent to annealing at 950 °C. A thermally activated solid state chemical reaction was shown to occur at the diamond/refractory metal interface. The products of the chemical reaction are difficult to remove by chemical etching. The annealed contacts provide a dramatic change in current flow (typically a factor of 10^{10} in lightly doped semiconducting diamond).

The reaction was characterized using I-V measurements, scanning electron microscopy, Auger electron spectroscopy, x-ray diffraction, and metallography. Utilization of these techniques showed that there is an optimal annealing time at 950 °C which produces a minimum in the electrical resistance of the contacts. The annealing regime was shown to be responsible for random nucleation and growth of molybdenum–carbide precipitates. Further, it was shown that the electrical conductance of the contacts was a function of the areal density of the precipitates at the original diamond/metal interface. Also, it was shown that the electrical resistance of the contacts began to increase as the carbide phase completely covered the original diamond/metal interface.

The results that were obtained for Mo, Mo/Au, and Mo/Ni/Au contacts to diamond were essentially the same, with the inference that the ⟨C⟩-Mo reaction at the interface is the principal factor in determining the properties of the contacts.

ACKNOWLEDGMENTS

We are indebted to our colleagues at the Naval Ocean Systems Center for their many contributions to the progress of this research. Special gratitude is due to Ken Regan, Dr. Howard Rast, Dr. Carl Zeisse, Maureen O'Brien, Dr. Don Mullin, Richard Nguyen, Paul Thibado, Dr. Charles Hewett, and Dr. Alan Gordon. We are also grateful to F. V. Thomas and D. B. King, Sandia National Laboratories, for providing us with the information on Table I. This work was supported by SDIO/IST through the Office of Naval Research under the direction of Max Yoder.

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APPENDIX B

TANTALUM OHMIC CONTACTS TO DIAMOND BY A SOLID STATE REACTION PROCESS

(Reference 2)

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TANTALUM OHMIC CONTACTS TO DIAMOND BY A SOLID STATE REACTION PROCESS

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INTRODUCTION

The recognized need for devices that can perform under severe operating conditions and recent advances in the growth of diamond films at moderate temperatures and low pressures has generated great interest in the exploitation of the many unique properties of diamond for solid state devices. Among these properties are high strength, high thermal conductivity, high band gap energy, high carrier mobility, and high resistance to degradation by exposure to radiation, heat, and corrosives [1,2].

Although ohmic contacts to natural and synthetic diamond had been produced for many years, the techniques employed, while satisfactory for research purposes, were not deemed suitable for large scale manufacturing. These techniques can be classified into four main categories, i.e. silver paint or tungsten probes on roughened or implanted surfaces [3-9], liquid phase reaction such as brazing [9-11], graphitization [11-13], and solid state reactions [1, 14-16]. Other techniques such as ion mixing have also been utilized [17].

In order to ensure that contributions of secondary factors, for example defects that might form during sputtering, etc. were minimized, the most benign technique for metallization to produce ohmic contacts, namely evaporation, was used in this study. Inasmuch as the techniques that were utilized and the results that were obtained in this study closely parallel those reported elsewhere [1] with molybdenum, molybdenum/gold, and molybdenum/nickel/gold; and in an earlier study with tantalum [14]; only a brief description of the experimental procedures will be provided below.

The diamond samples used in this study were naturally boron doped (p-type) semiconducting grade (Type IIb) with boron concentration of 10^{15} to 10^{16} per cm^3, carrier concentration of 10^{13} to 10^{13} per cm^3, and the dimensions of 5 mm by 5 mm by 1/4 mm. The samples were cleaned to remove organic surface contaminants and selectively metallized subsequent to masking the surface using slightly modified photolithographic techniques. The modification was required to accommodate exposure to high temperatures that were necessary to obtain adherent ohmic contacts to diamond [1]. The metallized regions were a series of rectangles 0.12 mm by 0.3 mm. The spacings between adjacent rectangular pads were 5, 10, 20, 30, and 50 micrometers in extent. Ten nm thick tantalum films were deposited onto the partially masked diamond surface using an electron beam evaporation source in an ion-pumped ultra-high vacuum system. A 150 nm thick gold film was evaporated on the tantalum surface to improve its resistance to corrosion. The samples were annealed at 950°C in a tube furnace in an atmosphere of flowing purified hydrogen gas. Room temperature resistances of adjacent metallized pads were measured prior to annealing and as a function of annealing time. The diamond/metal interfaces were characterized using Auger electron spectroscopy (AES), metallography, scanning electron microscopy (SEM), and X-ray diffraction (XRD).

RESULTS AND DISCUSSION

The room temperature resistance of adjacent metallized pads for each of the five specified pad spacings as a function of annealing time at 950°C is shown in Figure 1. This figure shows that the room temperature resistance between adjacent metallized pads decreases sharply, reaches a minimum value at approximately 1/2 hour, and increases slightly with increasing annealing time at 950°C. This behavior closely parallels the results that were obtained for metallized molybdenum, molybdenum/gold, and molybdenum/nickel/gold contacts to diamond and reported earlier [1], except that the minimum in room temperature resistance occurred at approximately six to eight minutes for diamond/molybdenum. This type of behavior is indicative of a chemical reaction and in this instance clearly an interfacial chemical reaction between diamond and tantalum is the most likely event. Consequently, the interfacial region was examined and characterized to determine the reaction product and the reaction product morphology. The techniques that were used for characterization included Auger electron spectroscopy, metallography, scanning electron microscopy, and X-ray diffraction. Figure 2 is a scanning electron micrograph of the diamond/tantalum interface after the metallized and annealed surface was etched to remove the metal deposit. The micrograph shows a large number of bright spots and dark spots, however, the dark spots are less noticeable in the reproduction of the micrograph than the bright spots. These spots are images of protrusions and of intrusions, respectively, relative to the planar surface topography. Similar results were also observed for a diamond surface metallized with molybdenum after annealing and etching. The major difference between the diamond surface metallized with molybdenum compared to the diamond surface metallized with tantalum is the relative size of the individual spots which appear to be larger for diamond/molybdenum contacts [1]. X-ray diffraction of the sample, prior to etching, as means of identifying the interfacial reaction products did not produce totally satisfactory results because of the extreme thinness of the film. However, Auger electron spectroscopy in conjunction with depth profiling from the vacuum/metal interface to the metal/diamond interface gave positive indication that the reaction product was a carbide of tantalum, as shown in Figure 3.

The Auger electron spectra has been used extensively and quite effectively to distinguish between graphitic carbon, diamond, and bound carbon in carbides [1,18,19]. As may be observed in Figure 3, the carbon spectra in the vicinity of the tantalum/diamond interface is indicative of carbon in the combined state, i.e. as tantalum carbide.

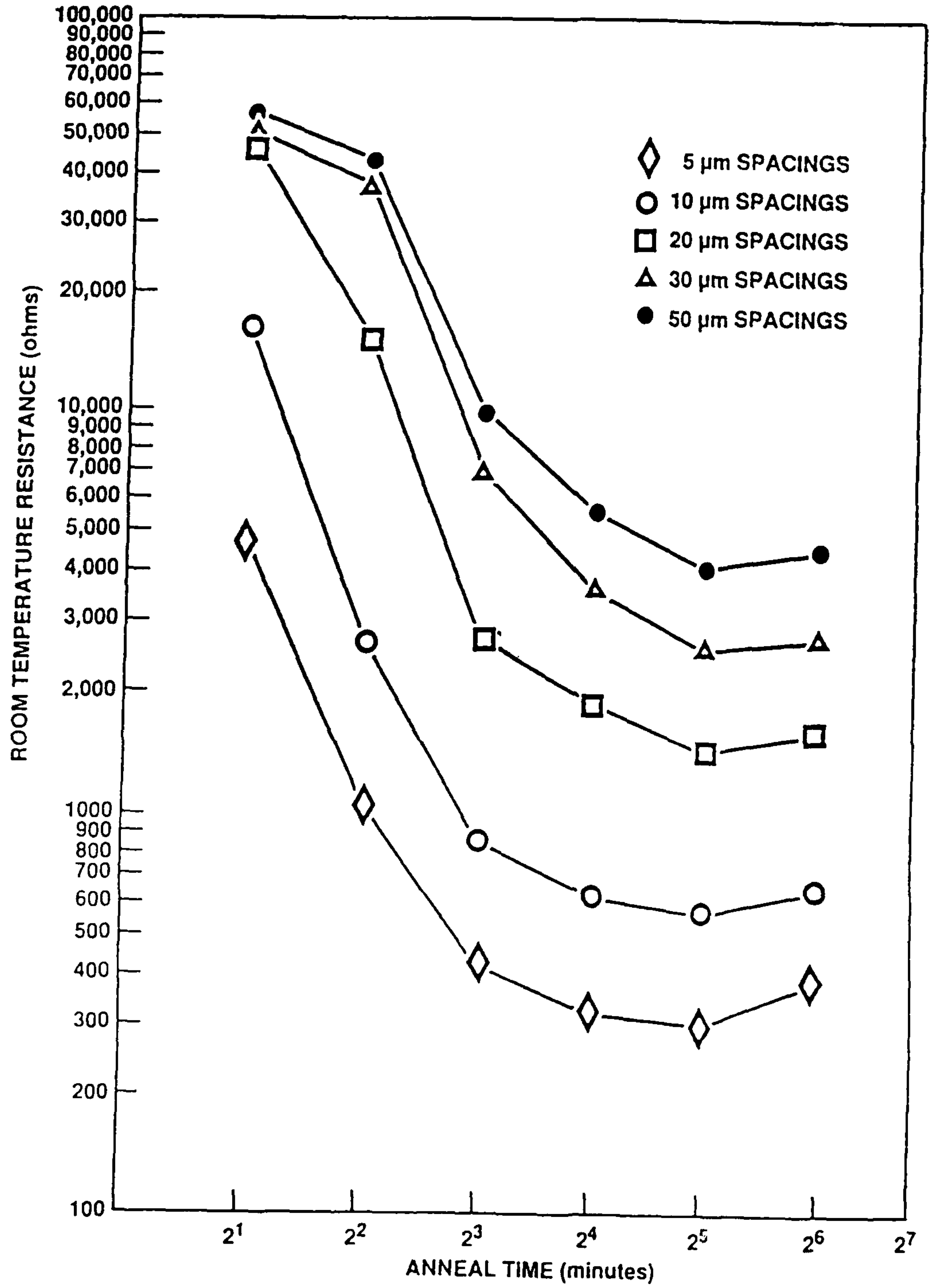

Figure 1. Room temperature resistance of metallized tantalum pads to diamond as a function of annealing time at 950°C.

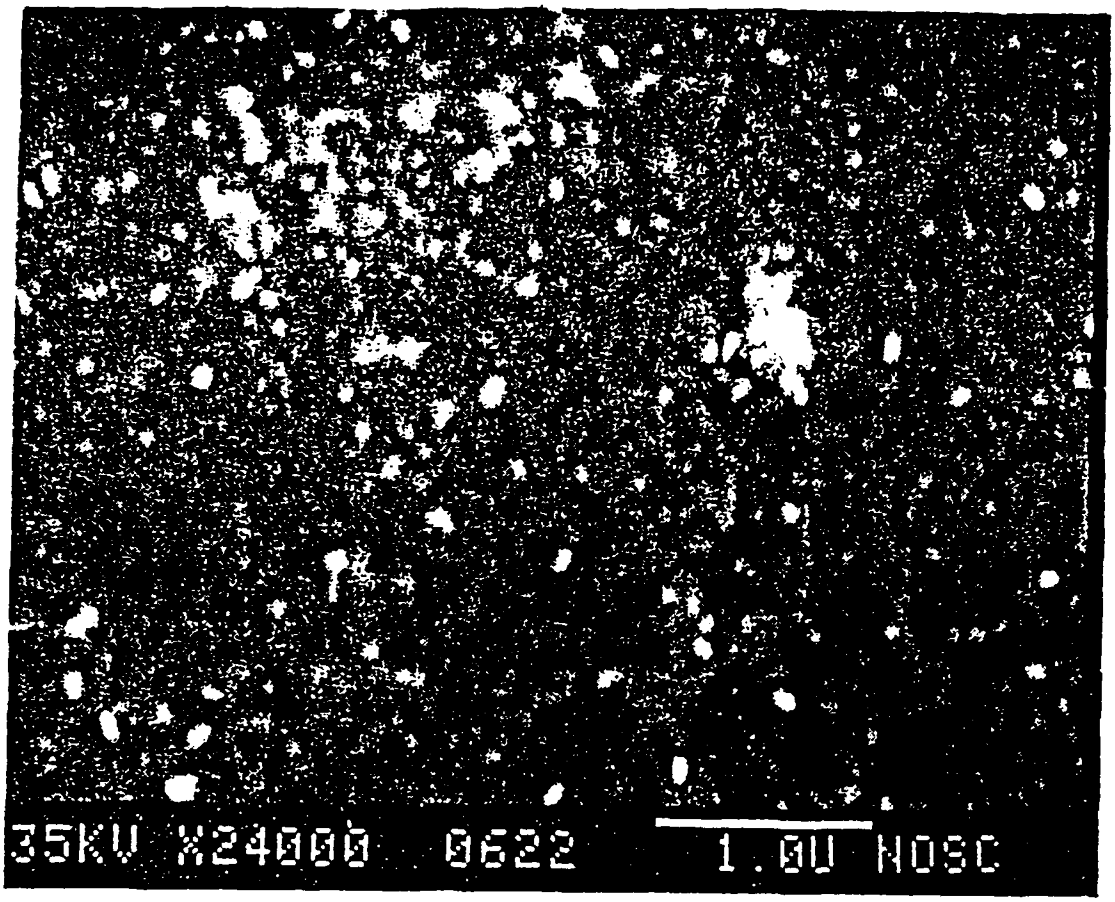

Figure 2. Scanning electron micrograph of the metallized and annealed diamond/tantalum interface subsequent to etching to remove the metal deposit.

Based on the results of the characterization studies of the interface, it may be postulated that tantalum reacts with the diamond at the diamond/metal interface. This reaction produces tantalum carbide precipitates by a nucleation and growth kinetic process. Further, the carbide precipitates grow in both the lateral and normal directions to the interface. Based on the analysis of the SEM micrograph of the interface, it may be concluded that the carbide precipitates grow into the diamond lattice, hence the source of the intrusions observed on the micrograph. Further, the precipitates grow into the metal film and the projection of these precipitates are observed as protrusions on the micrograph. The electrical response of the contacts as a function of annealing time may be justified based on the postulation that the sized, the shape, and the areal density of the carbide precipitate are the controlling factors in the electrical conduction of the contacts.

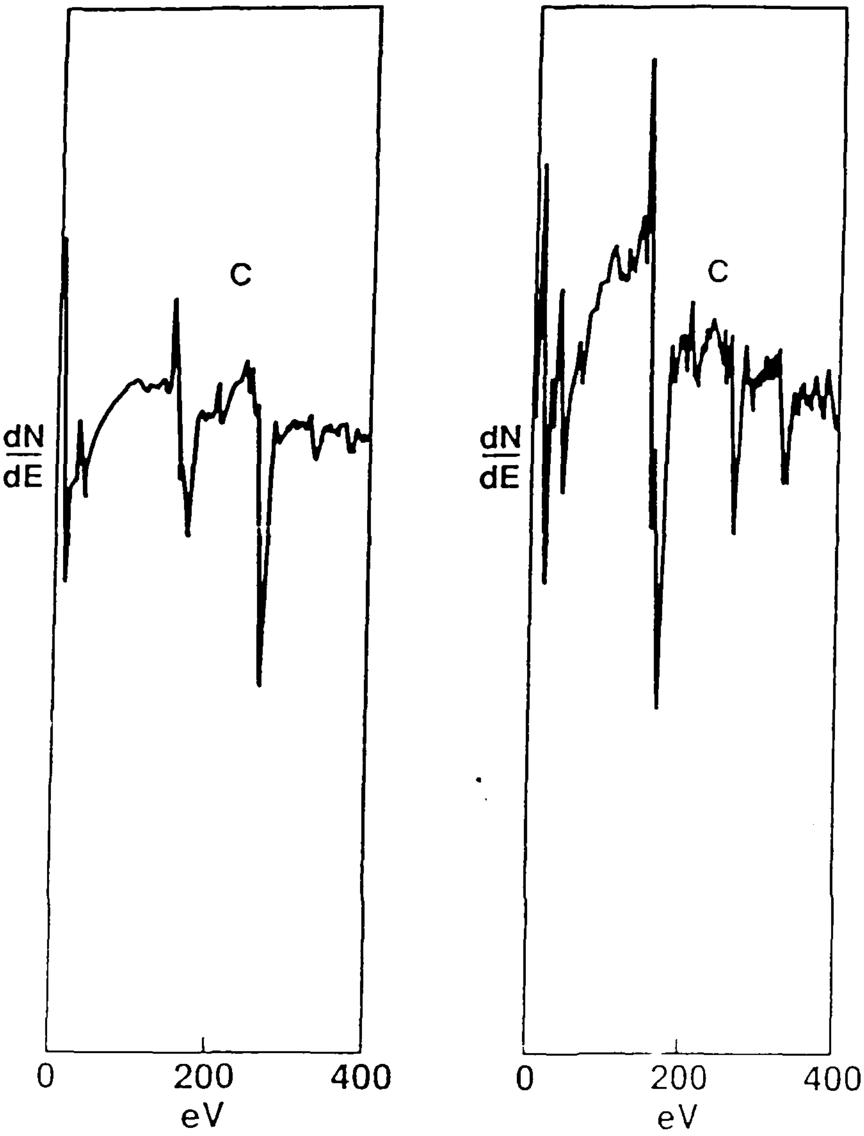

Figure 3. Auger electron spectra of a diamond/tantalum/gold sample after annealing and etching to remove the gold overlayer showing the vacuum/tantalum interface spectra (on the left) and the tantalum/diamond interface spectra (on the right). Note the marked difference in the carbon spectra in the 230-280 eV region.

The tantalum/gold contacts are tenaciously adherent to diamond as evidenced by the results of pull-test-to-failure of gold wires bonded to the contacts using an ultrasonic ball bonder. The test consisted of a pull test of 14 gold wire ball bonds to the metallized diamond contacts. In each instance, the wire fractured while the ball bond to the contact remained intact. The average value of the load to fracture the gold wire was 4.2 gm.

CONCLUSIONS

Tantalum films (10 nm thick) evaporated onto diamond single crystal surfaces were shown to produce ohmic contacts subsequent to annealing at 950°C. An evaporated gold film (150 nm in thickness) on the surface of the tantalum film decreases its susceptibility to corrosion. The annealed contacts have ohmic response and their room temperature electrical resistance decreases sharply with annealing time at 950°C. A minimum value for the room temperature electrical resistance was obtained for contacts annealed at 950°C for approximately 30 minutes. There was a slight increase in the electrical resistance as the time of annealing was increased further. The decrease in the resistance between pairs of contact pads after annealing was typically greater than ten orders of magnitude. The annealed contacts were characterized using Auger electron spectroscopy, metallography, scanning electron microscopy, and X-ray diffraction. The analysis of data obtained by these techniques established the presence of a carbide precipitate at the original tantalum/diamond interface. The ohmic contacts are adherent and gold wires were bonded to the contacts using an ultrasonic ball bonder. Pull-test-to-failure results indicated that the wires fractured while the bonds to the contacts remained intact. The tantalum ohmic contacts to diamond follow a similar reaction mechanism as those that were determined for molybdenum contacts to diamond [1], but the reaction rate was shown to be lower for tantalum than for molybdenum.

It is concluded that the formation of tantalum carbide at the diamond/tantalum interface is the principal factor for the formation of low resistance adherent ohmic contacts to diamond.

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APPENDIX C

METALLIZATION OF SEMICONDUCTING DIAMOND: Mo, Mo/Au, and Mo/Ni/Au

(Reference 3)

METALLIZATION OF SEMICONDUCTING DIAMOND: Mo, Mo/Au and Mo/Ni/Au.

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ABSTRACT

A processing technology has been developed to make ohmic contacts to naturally doped semiconducting diamond. The approach follows, as far as possible, conventional photolithographic techniques for metallization of semiconductors currently in use in the microelectronics industry.

Ohmic contacts have been successfully made to naturally doped semiconducting diamond using evaporated thin films of molybdenum, molybdenum/gold, and molybdenum/nickel/gold. The metal contacts form a tenacious bond with the diamond substrate after annealing. The time and the temperature of annealing also affects the type and the degree of conduction of the contacts.

Characterization of the interface of the metal contacts to diamond using AES, SIMS, RBS, XRD, SEM, and metallography clearly indicates that metal-carbide-precipitates nucleate and grow at the diamond/metal interface during annealing. It is concluded that the size and the areal density of the carbide precipitates at the interface are the principal factors that control the adhesion, and the mode and the degree of conductivity of the metal contacts.

Sponsorship of this research by SDIO/IST, ONR, and NOSC/IR is gratefully acknowledged.

INTRODUCTION

The goal of this research is to develop a technology to produce reliable, reproducible, low resistance ohmic contacts to thin films of epitaxial monocrystalline diamond. Implicit in this goal is the requirement that the techniques be compatible, as far as possible, with conventional manufacturing practice in the microelectronic industry. Further, it is assumed that the ohmic contacts to diamond are intended for diamond devices operating at temperatures exceeding 400° Celsius and in environments that are, very likely, corrosive and/or contain high levels of radiation.

Inasmuch as, epitaxially grown monocrystalline semiconducting films of diamond were unavailable at the inception of this research effort, naturally boron-doped semiconducting diamond samples were used in this study. The rationale being that the processes developed for producing ohmic contacts to natural diamond could be adapted to synthetically grown diamond films in a shorter time period than delaying the research until such time as synthetically grown films would be availabe for study.

Over the years, a number of investigators [1-3] have used a variety of techniques for making ohmic contacts to diamond. These techniques were found to be unsuitable for the present purposes; either because they are labor intensive, lack reproducibility, or can not withstand the rigors of the intended operating conditions cited above. More recently, an approach for making ohmic contacts that relies on "ion mixing" has been suggested [4]. While this approach is not beset with the shortcomings cited above, it does raise concern regarding the effect of the damage, introduced during implantation, on the physical and electrical properties of semiconducting diamond.

At the outset, it was postulated that both the adherence and the conductivity of the contacts were dependent on the formation of a primary chemical bond between the contacting material and the diamond. Consequently, the choice of the contacting material was limited to carbide forming metals. The requirement that the diamond devices, for which the ohmic contacts were being developed, were to be used at elevated temperatures further limited the choice of the contacting material to refractory or quasi-refractory carbide forming metals. It was recognized that these metals were susceptible to corrosion, consequently, in most instances, a layer of a noble metal such as gold was deposited on the "reactive" metal.

In a series of studies, a number of metal films including molybdenum, molybdenum/gold, molybdenum/nickel/gold, nickel, tantalum/gold, titanium/gold, and titanium platinum were investigated and the results reported elsewhere [5-7]. In this report, recent results that have been obtained with molybdenum, molybdenum/gold, and molybdenum/nickel/gold ohmic contacts to naturally doped diamond substrates will be discussed.

EXPERIMENTAL PROCEDURES

The diamond samples that were used in this study consisted of naturally boron-doped p-type semiconducting diamond (class IIb) with the dimensions of 5 x 5 x 1/4 mm or 4 x 4 x 1/4 mm. The boron concentrations were in low to mid 10E16 and carrier concentrations in high 10E13 to low 10E14.

Briefly, the experimental procedures consisted of cleaning the diamond substrates using decontam, Q-water, and ethanol, sequentially. The samples were then baked at 120° Celsius for 20 to 30 minutes and loaded into an ion-pumped ultra-high vacuum system. The diamond samples were metallized using either an electron beam evaporation source (for metals having melting temperatures exceeding 1500° Celsius) or by using a resistively heated evaporation source (for metals having melting temperatures below 1500° Celsius). The thickness of the deposited "carbide forming" metals had a range of 5 to 25 nm, whereas, the noble metal films had a range of 150 to 500 nm in thickness. Multicomponent films were usually deposited, in situ, sequentially to produce an abrupt interface and to minimize alloying, although on several occasions, graded interfaces were produced by simultaneous evaporation of two metals to determine if this factor affected the adhesion of the films.

Following deposition, the metallized samples were baked at 120° Celsius for approximately 20 to 30 minutes and then annealed, usually, in a tube furnace in an atmosphere of purified hydrogen gas. Some of the samples were also annealed in a rapid thermal annealing (RTA) furnace to determine the most suitable annealing regime.

Current-voltage characteristics were measured, usually, on a curve tracer. Materials characterization consisted of Auger electron spectroscopy (AES), Rutherford backscattering spectroscopy (RBS), secondary ion mass spectroscopy (SIMS), galvanomagnetic measurements, scanning electron microscopy (SEM), x-ray diffraction (XRD), and metallography.

The specific procedures used in producing ohmic contacts to natural diamond substrates using molybdenum, molybdenum/gold, and molybdenum/nickel/gold films were: a) Deposited molybdenum films with thickness of 5 to 25 nm using an electron beam vaporization source. b) Deposited nickel films with thickness of 15 to 25 nm. c) Deposited gold films with thickness of 150 to 250 nm using resistively heated vaporization source. d) Baked samples at 120° Celsius for 20 minutes. e) Annealed samples at 950 ± 10° Celsius for various times from 30 seconds to 16 minutes. f) Measured the I-V response as a function of annealing time. g) Characterized the diamond/metal interface.

RESULTS AND DISCUSSION

As has been reported earlier [5-7], the electrical response of the annealed samples exhibited a sharp decrease in resistance (exceeding ten orders of magnitude) relative to the as-received and the metallized samples prior to annealing. Further, the I-V characteristics of the annealed samples exhibited a linear relationship between the applied potential and the current flow over a wide range of applied potentials. Moreover, the resistance of the contacts was strongly dependent on the time and the temperature of annealing. The resistance of the contacts decreased sharply with annealing time to a minimum value at 6 to 8 minutes and increased slightly as the time increased beyond 8 to 10 minutes. The minimum resistance attained was approximately 500 ohms for contact pads with separation distance of 5 μm.

SIMS and RBS examination of the metallized samples indicated that molybdenum had penetrated into the diamond substrate during annealing. Metallographic and SEM examination of the metallized and annealed samples revealed the presence of precipitates at the diamond/metal interface. AES analysis indicated that the "shoulder" preceding the main carbon KLL transition line (nominally at 270 eV) changed its shape from that associated with adsorbed carbon to that associated with carbon compounds to that associated with diamond as depth profiling was effected from the air/metal interface through the metal/diamond interface. XRD studies of the annealed molybdenum, and molybdenum/gold contacts established that the precipitate at the diamond/metal interface is a carbide of molybdenum with a high degree of preferred orientation as evidenced by the presence of a single dominant peak at $2\theta \approx 37.8^\circ$. Due to the extreme thinness of the films, it was not possible to differentiate between Mo_2C and $Mo_{24}C_{58}$.

The formation of the molybdenum carbide precipitates at the metal/diamond interface, as shown in Figure 1, is thought to be responsible for the dramatic change in the electrical response of, and the tenacious adherence of the annealed metal contacts to diamond. The tenacity of the contacts is demonstrated by the ability to attach adherent gold wires to the metallized diamond samples by an ultrasonic wire bonding process, as shown in Figure 2. The 5 x 5 x 1/4 mm diamond sample was lifted by the gold wire and the bonds supported its total weight.

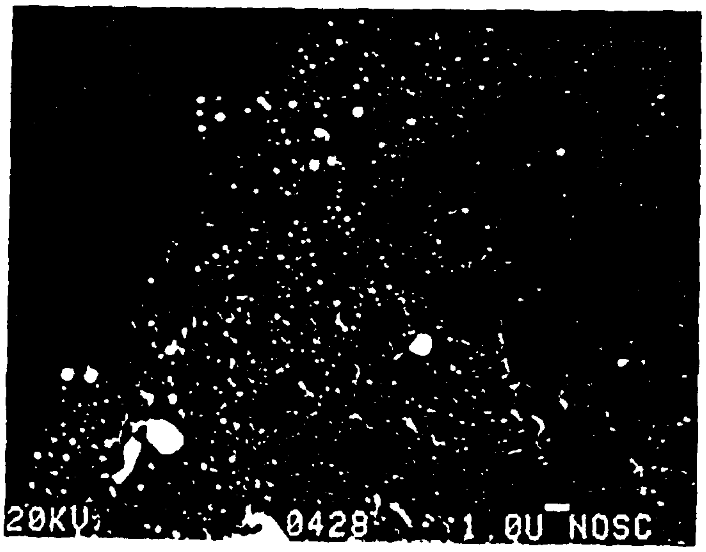

Figure 1. SEM micrograph of molybdenum/gold contact to diamond after annealing and etching to remove the excess metal.

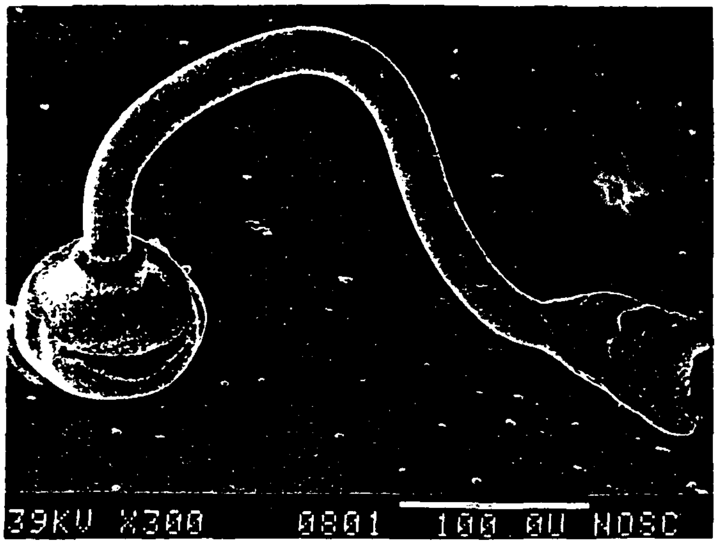

Figure 2. A scanning electron micrograph of a ball and a wedge bond to a molybdenum/gold contact to a diamond substrate.

CONCLUSIONS

During annealing of molybdenum, and molybdenum/gold contacts to naturally doped semiconducting diamond, a molybdenum carbide precipitate nucleates and grows at the diamond/metal interface. The electrical response of the contacts is a function of size and areal density of the precipitates. The electrical resistance of the contacts reaches a minimum value prior to the formation of a monolithic carbide phase at the interface.

ACKNOWLEDGEMENTS

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APPENDIX D

SPECIFIC CONTACT RESISTANCE MEASURMENTS OF OHMIC CONTACTS TO DIAMOND

(Reference 4)

To be published in the procedings of the Second International Conference on the New Diamond Science and Technology

Specific Contact Resistance Measurements of Ohmic Contacts to Diamond

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ABSTRACT

We have demonstrated the applicability of the specific contact resistance measurement scheme of Reeves [1] to semiconducting diamond. Four sample types were used: highly doped epitaxial films on <100> and <110> type IIa substrates; a type IIb diamond 0.25 mm thick, and a type IIb diamond 0.05 mm thick. Measured specific contact resistances ranged from $2x10^{-5}$ to $1x10^{-2}$ ohm-cm^2.

INTRODUCTION

The unique material and electronic properties of diamond make it a potentially very important candidate for use in high power or high frequency applications, as well as in high temperature and corrosive environments. Several authors have recently reviewed the motivation and prospects for semiconducting diamond based electronic devices [2-4]. While several critical areas for research were identified, we note that progress has been made in key areas. The growth of large homo-epitaxial films doped with boron, a major step toward the growth of single crystal diamond films on substrates other than diamond, has been reported [3-7]. Regrowth of radiation damage layers careated by ion implantation in diamond has also been reported [8]. Success in forming electrical contacts (both rectifying and ohmic) to diamond has also been reported in the literature [9-12]. In this paper measurements of the specific conatact resistance of ohmic contacts to diamond are presented.

Ohmic contacts are characterized by measuring the series resistance arising at the contact-semiconductor junction, R_C. Normalizing the contact resistance to the contact area gives rise to the specific contact resistance, r_C. For the ideal case of uniform current flow perpendicular to the contact we have $r_C=R_C/A$, where A is the contact area. In reality, however, the current flow is rarely perpendicular, and the finite resistance of the semiconductor leads to current crowding [13-15]. Measurement techniques have been developed to allow the current crowding and bulk resistance of the semiconductor to be deconvolved from R_C, thereby uniquely determining the specific contact resistance [15-16]. Conceptually, the simplest technique is that of Cox and Strack [16], in which contacts are made to both the front and back sides of the sample. The primary advantages of this technique are the ease in processing the contacts and the simplified analysis due to the geometry. However, due to the semi-insulating nature of bulk diamond, there is a large series resistance contribution to the total resistance from the substrate itself. Thus, in order to determine the specific contact resistance one is forced to take the difference of two (nearly equal) large numbers. A second technique utilizes an array of contact pads of equal size, but varying separation contacting a thin conducting layer. The contact resistance in these structures is analyzed using the transmission line model [15]. The primary drawback to transmission line model measurements is the need to perform a mesa etch in order to reduce the analysis of current flow between contacts to a two dimensional problem.

Two techniques for eliminating the mesa etch requirement from the transmission line model measurement have been demonstrated [1,17]. One approach [17] is to simply extend the contact pads across the width of the sample, forming an array of contact lines. The second approach is to use a circular test pattern consisting of a central dot and concentric ring contacts. The measurements are interpreted using a circular transmission line model. For two reasons we judge the second approach to be superior to the first in analyzing diamond samples. First, the use of contact lines requires rectangular (or square) samples and is not adaptable to samples of irregular shape. Second, natural diamonds are frequently non-uniformly doped and the use of circular contacts permits probing over a smaller area. Thus, we chose the circular transmission line model for determining r_C. For the details of the analysis, the reader is referred to reference [1].

Several constraints must be placed on ohmic contacts to diamond. First, they should have a low contact resistance. Second, they should be able to withstand the operating conditions for which diamond devices are intended; e.g. high temperatures. Third, they should be strongly adherent to the diamond surface. Fourth, they should be compatible with conventional device processing techniques. Ohmic contacts produced via a solid state annealing process have been studied extensively and are believed to satisfy all four conditions [9]. In this process a thin film of a transition metal carbide forming metal is deposited on the diamond surface. Annealing at high temperature (950 C) leads to the formation of a carbide layer at the interface. This layer provides an intimate contact to the diamond and promotes good adhesion. Figure 1 shows the resistance measured between two Molybdenum-diamond contacts as a function of annealing time at 950 C in hydrogen. From the figure it is clear that annealing the contact produced a decrease in total resistance of several orders of magnitude. Auger electron spectroscopy studies indicated that the decrease was associated with the formation of a carbide phase. Similar results have been observed for Ti and Ta contacts. Measurements of the specific contact resistance are required in order to determine the metallizations that provide the lowest electrical impedance for device applications.

EXPERIMENTAL PROCEDURE

Four different diamond samples were used in this study. The first sample consisted of a diamond film with a high boron concentration and about 4 microns in thickness grown epitaxially on a <100> type IIa insulating diamond substrate with the dimensions of 5 x 5 x 0.25 mm. The second sample consisted of a 6 micron thick diamond film with a high boron concentration grown epitaxially on a <110> substrate. These films were grown by Dr.

Michael Geis using the procedure outlined in [6] on natural diamond substrates provided by Dr. Michael Seal. The third sample was an irregularly shaped type IIb diamond 0.25 mm thick. The fourth sample was identical to the third, except that it had been thinned to 50 microns in thickness.

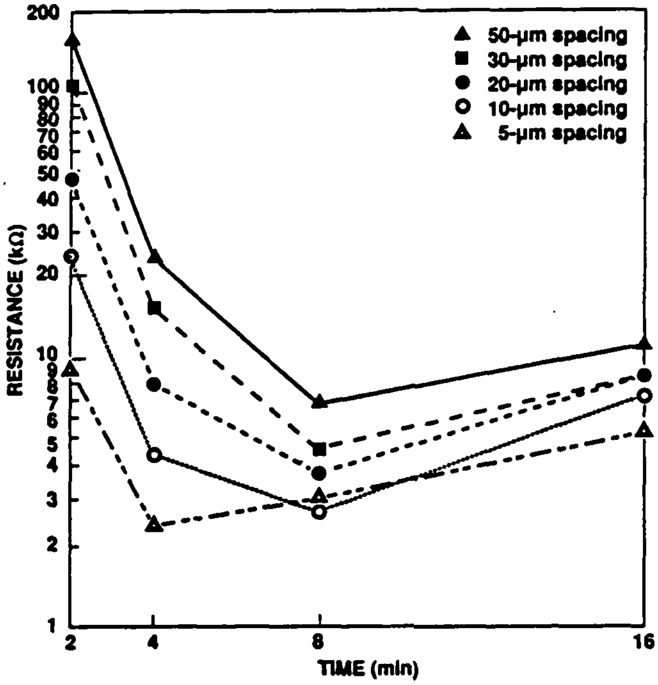

Figure 1 Resistance between two Mo/diamond contacts as a function of annealing time at 950 C in an H_2 ambient.

The samples were cleaned using decontam, deionized water, and ethanol, sequentially. The samples were then coated with photoresist and patterned using standard photolithographic techniques. Samples were baked at 120 C for 20 minutes following photoresist patterning and loaded into an ion pumped ultra-high vacuum system (base pressure 5 x 10^{-9} Torr). Electron beam evaporation was used for deposition of the carbide forming metal (either Ti or Mo). The thickness of the carbide forming metal was about 100 Å. Subsequently, 1500 Å of Au was deposited from a resistively heated boat onto the surface of the Ti or Mo without breaking vacuum to prevent oxidation prior to annealing. The pressure during evaporation was 2 x 10^{-7} Torr. Film thicknesses were determined using a crystal monitor during deposition. After deposition a lift-off process was used to remove undesired metal, leaving contact structures with the geometry shown in figure 2. The dimensions (in the notation of Reeves) were $r_1'=1.65r_0$, $r_1=2.74r_0$, $r_2'=4.34r_0$, and $r_2=5.45r_0$ with r_0 =11.7 microns.

Following patterning, the contact structures were probed using a Keithley model 220 current source and model 196 DMM. After probing, the samples were baked at 120 C for approximately 20 minutes and then annealed in a purified hydrogen ambient at 950 C. Anneal times were 2 minutes for Ti and 6 minutes for Mo. After annealing, the samples were remeasured.

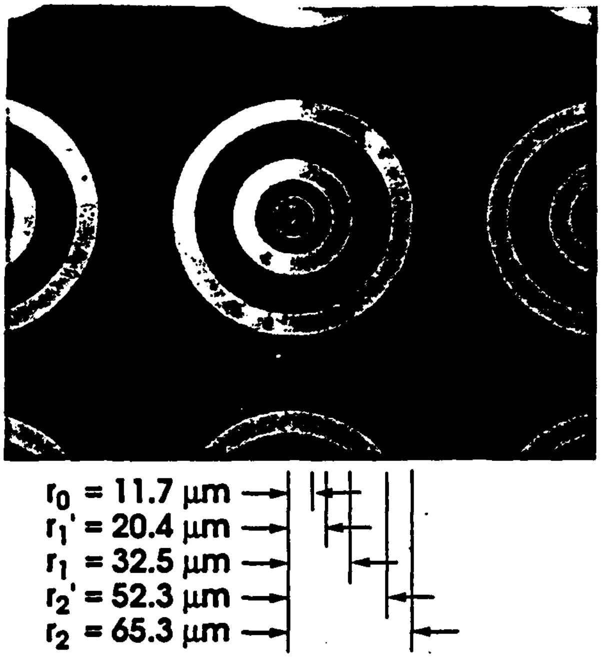

Figure 2 Circular contact pattern used for this work. The dimensions are $r_1'=1.65r_0$, $r_1=2.74r_0$, $r_2'=4.34r_0$, and $r_2=5.45r_0$ with $r_0=11.7$ microns.

The measurements consisted of placing tungsten probes on the inner dot, the central ring and the outer ring. The total resistance between the central ring and the inner dot, and the central ring and the outer ring were measured. The end resistance was determined by passing a current through the central ring and the inner dot and measuring the voltage between the central ring and the outer contact. This result was checked by switching contact pairs and remeasuring. Using these three results, the specific contact resistance can be calculated in the manner of [1].

RESULTS AND DISCUSSION

Ohmic contacts between a metal and a semiconductor may be formed either by lowering the effective barrier height, or by heavily doping the semiconductor at the interface. Heavily doping the semiconductor induces a decrease in barrier thickness, allowing tunneling of the charge carriers. Lowering the barrier height is difficult since diamond has a barrier height essentially independent of the metal work function [18]. Increasing the doping in natural semiconducting diamond is a non-trivial task, but may be accomplished rather easily during epitaxial growth of diamond. Table I shows the values of specific contact resistance determined in this experiment. It is interesting to note that contacts to the epitaxial layers (epi-<100> and epi-<110>) showed excellent behavior as deposited. Contacts formed by placing tungsten probe tips on the diamond surface showed only a slight deviation from linearity. Contacts formed by the Ti films were highly linear. This may be due to the highly doped nature of these layers. The measured value of specific contact resistances after annealing are more than satisfactory for device fabrication. Lightly doped diamond (represented by the "thin" and "thick" samples) are much more difficult to contact. Non-ohmic behavior was observed for the as-deposited contacts in these samples.

Several factors influence the accuracy of these measurements. Of primary importance is the thickness of the conducting layer. Correct interpretation of the transmission line measurements requires that current flow between contact pads be two dimensional, i.e., no vertical flow of current in the diamond. For the epitaxial layers this condition may be assumed to be approximately true. For the 50 micron and 250 micron (bulk) layers, however, there is almost certainly a large component of vertical current flow in the sample. This adds a large spreading resistance term to the overall contact resistance, which in turn greatly adds to the complexity of the transmission line analysis. The possibility of using an approximate geometric correction factor for the thickness of the diamond is being explored.

Table I
Specific Contact Resistance Results for Various Samples

Sample	Conducting Layer thickness (um)	Metal	N_A (cm^{-3}) at 300 K	r_c ($\Omega-cm^2$) As-deposited	r_c ($\Omega-cm^2$) Post Anneal
epi-<100>	4	Ti	$2x10^{19}$	$3.2x10^{-6}$	$1.8x10^{-5}$
epi-<110>	6	Ti	$7x10^{19}$	$7.6x10^{-5}$	$2x10^{-5}$
thin	50	Mo	(a) 10^{14}	over-ranged	$1.2x10^{-3}$
thick	250	Mo	(a) 10^{14}	over-ranged	$1.4x10^{-2}$

(a) Representative value from other type IIb diamond samples.

It is also of interest to note the specific contact resistance of the SiC and Ta carbide contacts studied by Fang, et al [11]. They obtained an average value of about 1 x 10^{-3} ohm-cm^2 for both cases. The conventional linear transmission line was used in their study leading to the necessity of forming a mesa. This was accomplished using a CF_4 plasma etch. A thin conducting layer was formed by inducing ion damage in the diamond. Thus the difference in r_c between the two studies may be due a difference in doping level, a difference in contacting lightly damaged diamond versus undamaged diamond, or an effect of the plasma etch.

CONCLUSIONS

Specific contact resistance for the Ti and Mo refractory metal carbide contacts to diamond have been measured. The values determined from the contacts to the bulk type IIb diamond samples are in reasonable agreement with those published previously [11] for SiC or Ta carbide contacts, indicating the usefulness of the circular transmission line model in avoiding a mesa etch and allowing specific contact resistances to be easily determined.

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APPENDIX E

ELECTRICAL ACTIVATION OF BORON IMPLANTED INTO DIAMOND

(Reference 5)

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ELECTRICAL ACTIVATION OF BORON IMPLANTED INTO DIAMOND

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ABSTRACT

A natural IIa diamond was implanted with boron ions at a substrate temperature of 80 K. Ohmic contacts (Mo/Au) were made to the unimplanted side using a solid state reaction process. Gold wires were then bonded to the contacts for Van der Pauw/Hall measurements as a function of temperature from room temperature to nearly 600°C. Contacts were removed and the procedure repeated for the implanted side. Resistivity stabilization occurred at approximately 350°C to over 3.4 MΩ/square and 1.3 MΩ/square for the unimplanted and implanted sides respectively. The effect of the implant was evaluated on the basis of the relative difference in the resistivities, mobilities, and carrier concentrations between the implanted and the unimplanted sides.

INTRODUCTION

The unique properties of diamond relative to the semi-conductors 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 [1]. Ion implantation, an invaluable technique which has been used extensively with other semiconductors to place layers of n or p-type material at specific depths during different stages of the processing, has yielded inconsistent results [2]. These results are complicated by the ability of the implantation to produce damaged, graphitized 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 some critical value, while below this value, a significant portion can be repaired [2,3,4].

Studies on the effect of implantation in diamond have been further complicated by the wide differences in the characteristics of natural diamond. Additionally, recent papers have questioned the role hydrogen plays in the resistivity of diamond, with reported large changes in the resistivity, downward by annealing in nitrogen after plasma chemical vapor deposition growth (with hydrogen) [5], or upward by exposure of type Ia synthetic and type IIb natural diamonds to hydrogen plasma [6]. Previous work has shown that adsorbed gases play a significant role in terminating dangling bonds on the diamond surface [7,8]. Also, diamond has photoconductive properties [9] which could introduce low level background currents. Nonetheless, many authors have tried to make conclusions based upon comparison between two different diamond samples, one implanted, one not.

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

EXPERIMENTAL

Our starting material was a slice of natural type IIa diamond polished on both sides, 5x5 mm square, 0.25 mm thick. One side was successively implanted at a temperature of 80K with boron ions at three different energies and respective doses: 25keV (1.5 x $10^{14}/cm^2$), 50keV (2.1 x $10^{14}/cm^2$), and 100keV (3 x $10^{14}/cm^2$). A simulation of these implants gave projected ranges of 792±218Å, 1538±336Å, and 2901±483Å respectively. An experimental study of the depth distributions and range parameters for several elements including boron implanted into diamond based on SIMS measurements can be found in ref. [10], and indicate even smaller projected ranges. This combination of doses was expected to produce a fairly uniform implanted layer of between 0.2μm and 0.3μm in depth, below the critical dose for graphitization. After implantation, the sample was immediately removed from the cold stage and transferred to a pre-heated furnace and annealed in a dry nitrogen ambient at 990°C for 10 minutes.

Next the sample was thoroughly cleaned in a saturated, boiling solution of Cr_2O_3 in H_2SO_4 at about 160°C for 10 minutes, and rinsed in de-ionized water. This was followed by a 10 minute dip in a boiling 50/50 solution of NH_4OH:H_2O_2 (30% stock solution) and a subsequent de-ionized water rinse. This sequence has been shown to remove old metallizations from prior depositions and is believed to successfully remove any graphitized layer that might have formed during the anneal or other processing steps. After a nitrogen blow dry, the sample was loaded into a holder for ohmic contact metallization which incorporated a stainless steel shadow mask with four small symmetric holes near the four corners of the sample for forming the proper Van der Pauw geometry. This assembly was then loaded into a UHV electron beam evaporating chamber and brought to vacuum. A Mo/Au (100Å/1500Å) layer was then deposited. After removal from the system, the sample was placed in a furnace and annealed for 6 minutes at 950°C in a H_2 environment. 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, the above procedure was used to place ohmic contacts on the unimplanted side of the diamond. The sample was then placed in a standard ceramic (alumina) 24 pin chip carrier (non-magnetic 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 using 10 minutes each of boiling trichloroethane, cold acetone, and boiling methanol. Additionally, the sapphire pieces were subjected to 5-10 minutes of 1:1:3 H_2SO_4:H_2O_2:H_2O, followed by 5-10 minutes of 1:1:25 NH_4OH:H_2O_2:H_2O. Each of the four contact pads on the diamond was then wire bonded to the appropriate contacts on the carrier, which was then placed in our high temperature Van der Pauw/ Hall Effect measurement apparatus, diagramed in fig. 1 below.

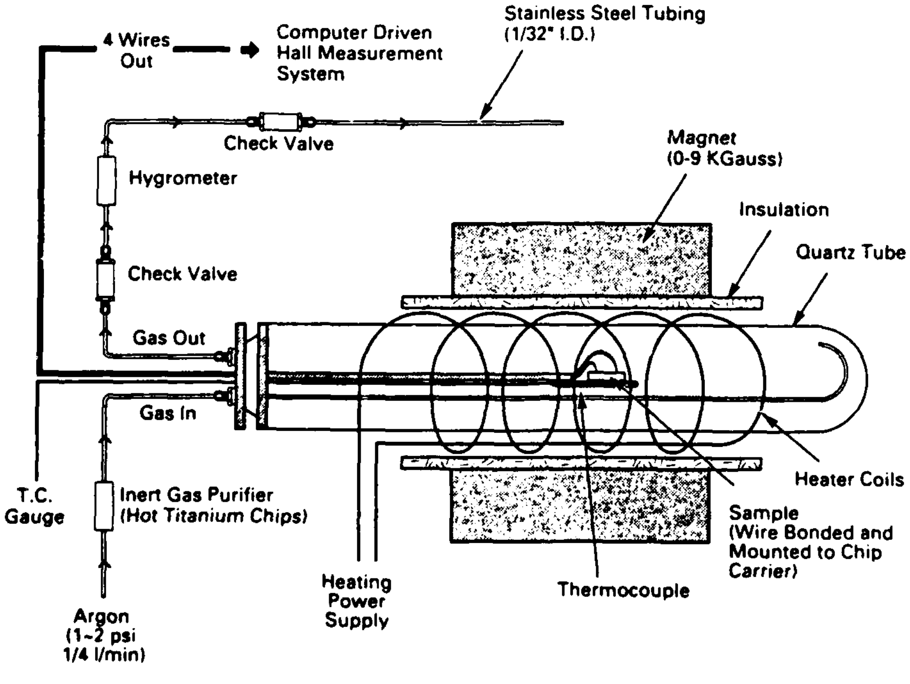

Fig. 1. Schematic diagram of the Hall Effect measurement system.

A few remarks should be made about the difficulties experienced in the design and operation of such a system. Firstly, we did not wish to have any extraneous gases reacting with the surface of the diamond. At high temperature, under atmospheric pressure, diamond will convert back to the graphitic phase of carbon, especially in the presence of oxygen or water vapor. Also, as mentioned earlier, there is some question as to the electrical role of other adsorbed gases into the bulk or surface. Thus, care was taken to insure that the atmosphere which the diamond saw at high temperature was only argon. A flow of 1/4 liter/minute of ultra-high 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. Baked (under argon flow just prior to ramping up the temperature) stainless steel tubing was used between the purifier and the quartz chamber used for the experiment. Two check valves and two sections of very small diameter stainless tubing were used to prevent air from getting back into the system through the gas exit port, and also 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 read off scale at a value less than -115°C.) Additionally, the system was leak checked under pressure, just prior to the experiment, with Snoop™.

Using this Van der Pauw geometry with the four ohmic contacts placed symmetrically on the corners of the sample, the resistivity was measured using the standard Van der Pauw technique by passing current through two adjacent contacts and measuring the voltage generated across the other two [12]. Homogeneity (uniformity of current flow) of the sample can be gauged by the form factor f (≤1.00), a function of the difference in resistivity obtained when the current is passed through contacts at 90 degrees from the previous measurement [13]. Ideally, this form factor should be equal to 1.00 for a homogeneous square sample with perfect ohmic contacts, and can be used as a gauge of the quality of the data. Under the influence of a perpendicular magnetic field, voltages generated in contacts diagonally opposed when current is passed through the other two allow for the measurement of the Hall coefficient and thus the mobility of the carriers and their concentration. Again, the homogeneity of the results can be gathered by remeasurement, this time switching sets of contacts and comparing the Hall voltages generated. The percent difference between the two measurements can also be an indication of the quality (and error) inherent in the data.

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 minutes (and at the same intervals for the second part of this experiment), a complete Van der Pauw/Hall measurement was completed at three different currents (4 μA, 10 μA, and 100 μA), each at three different magnetic fields (approx. 1800, 5200, and 8600 Gauss). High resistivity conditions caused us to not attempt the 100 μA current level when the supply voltage approached 100 V, near the compliance limit of our current source.

After the measurement was complete, the sample was removed from the system, and the diamond removed from the chip carrier. The diamond sample and the sapphire pieces were re-cleaned, using the same procedure used initially. This removed all the prior ohmic contact metallization. Ohmic contacts were then fabricated on the implanted side in the same manner as before, and identical van der Pauw/Hall measurements were performed as a function of temperature.

Diamond temperature was measured from a thermocouple junction on the other side of the chip carrier. The thermocouple was not in direct thermal contact with the sample. Consequently, the measured temperature is probably most characteristic of the ambient argon. Thus, in addition to making measurements only after allowing the thermocouple temperature to stabilize, we took the added precaution in this comparison to duplicate the ramp-up conditions between the two runs as closely as possible by using the same heater currents vs. time.

RESULTS AND DISCUSSION

The initial room temperature resistivities of the diamond sample in the argon ambient were unusually low, ranging from 62kΩ/square for the unimplanted side to 140kΩ/square 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/square for the implanted side and about 1.4 MΩ/square for the unimplanted side after about an hour. Further heating to 350°C produced a much more stable value of 3.4 MΩ/square for the unimplanted side, and 1.3 MΩ/square for the implanted side (at 350°C.) One possible explanation is that the H_2 introduced in the annealing step began to come out of the diamond, and that the difference in the resistivity caused by the implant only became measurable after this hydrogen had diffused out of the diamond.

After stabilization, the temperature of the diamond was reduced and further data was taken as a function of temperature as the temperature was again raised, but this time to nearly 600°C. A minimum of 20 minutes was allowed between changes in the heater current and each measurement. In contrast to the data taken prior to stabilization,these data did not change appreciably with time after the thermocouple reading stabilized. The only Hall/van der Pauw and resistivity data considered in evaluating the effect of the implanted boron ions, are those obtained after stabilization.

Fig. 2 shows the comparison of the resistivity data of the two sides as a function of inverse temperature. Only data which were sufficiently homogeneous to give a form factor of greater than 0.95 were accepted. Other authors have attempted to define a carrier activation energy from the log plot of the resistivity vs. inverse temperature [2,14]. However, the resistivity includes separate contributions from both the carrier concentration and the carrier mobility. It has been shown that the temperature dependance of the mobility can be significant.[15,4,16,17,18]

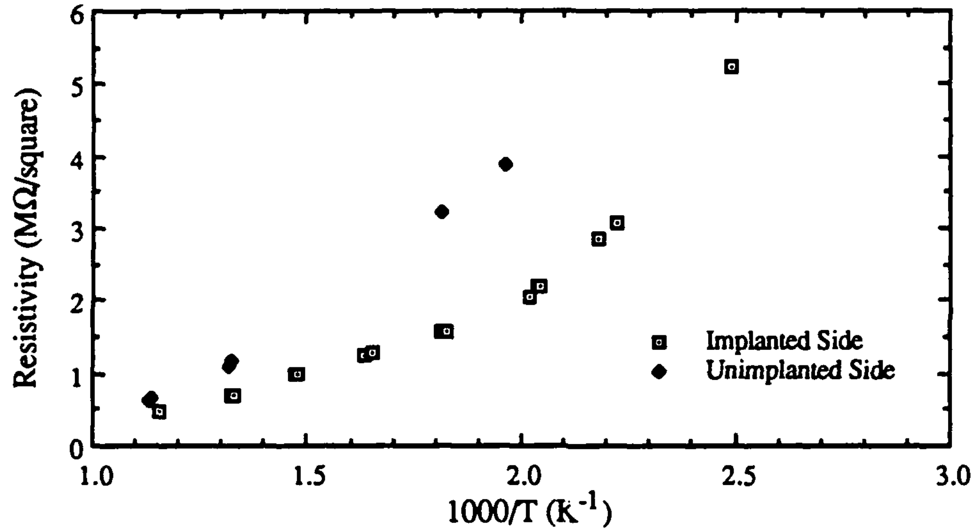

Fig. 2. Comparison between the implanted and unimplanted side resistivities vs. temperature after stabilization has occurred.

The carrier activation energy is derived directly from plots of the hole concentration (p) vs. inverse temperature. Here, the activation energy for the carriers is proportional to the slope if one assumes an Arrhenius type functionality:

$$p = N_A e^{-(E_A / kT)} \quad ; \quad E_A = -k \frac{d[\ln (p)]}{d[\frac{1}{T}]}$$

Fig. 3 shows the log of the carrier (hole) concentration plotted against the inverse temperature for the implanted side. Note that we have subscribed to the constraint suggested by the ASTM standard that the difference in the two Hall voltages be no more than ±10% of each other, for the Hall data to be declared valid. The slope obtained implies an activation energy for the boron implant of 0.29±.04eV. Plotted in fig. 4 is the measured mobility as a function of inverse temperature for the implanted side. The corresponding measured mobilities for the unimplanted backside (determined directly from Hall potentials that are for the most part too small to be measured accurately) are scattered widely around 3-5 cm^2/V-sec, occasionally reach negative values, and in almost all cases do not meet the ASTM standards. The values of p, which are inversely proportional to the resistivity and these mobilities, become even more scattered. This is the same situation that one might expect if there was a very small net carrier concentration on the backside.

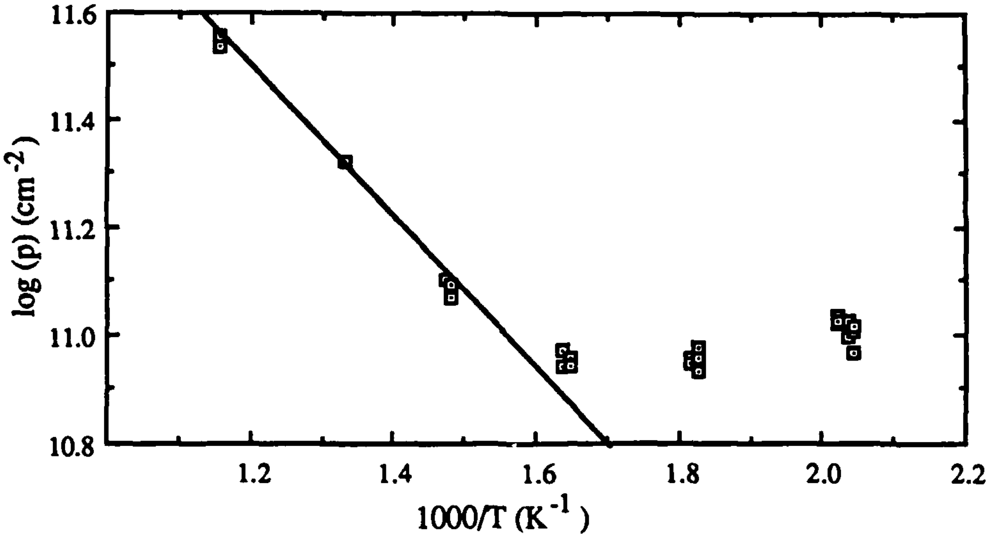

Fig 3. Log of the free carrier concentration vs. inverse temperature for the implanted side. The slope obtained implies an activation energy for the carriers of between 0.29±.04eV.

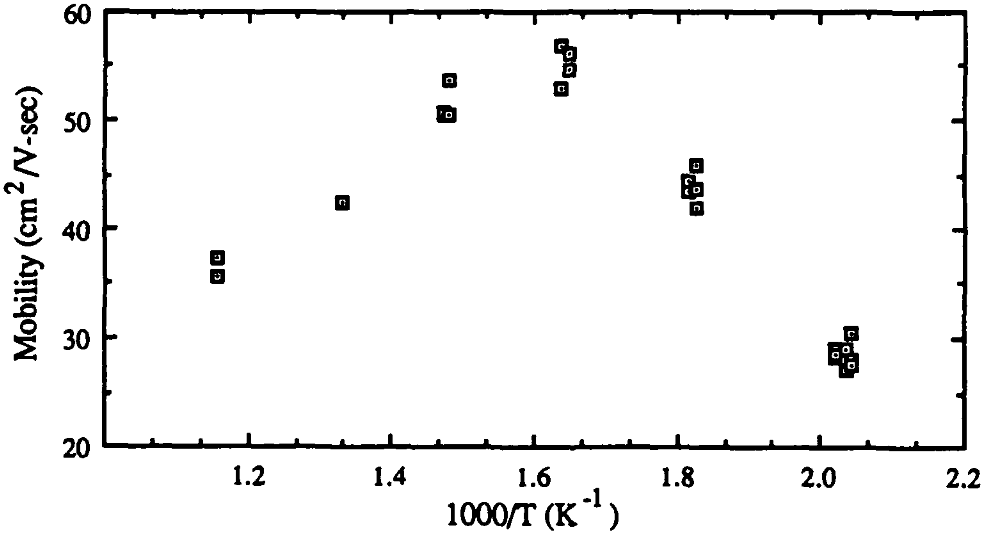

Fig 4. Measured mobility as a function of inverse temperature for the implanted side.

In order to verify system integrity, measurements were completed on another piece of natural IIb (boron doped) diamond. The measured free hole concentration, p, gave a hole activation energy of about 0.33eV, in excellent agreement with previous measurements [19] with a mobility of 400 cm^2/V-sec at 300 K that was lower than that reported by Collins [19], but within the range reported for synthetic diamond by other researchers [15,16].

CONCLUSIONS

By comparing the electrical transport properties 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, the effect of the implant was observed. The effect of the implant was seen both in decreased resistance, meaningful mobility results, and an acceptor activation energy derived from the carrier concentration of 0.29±.04eV.

Prior to measuring either side of the diamond, it was found that the diamond had to be preheated to a temperature of over 300°C for nearly an hour. During this time the resistivity of the diamond increased by nearly two orders of magnitude, and stabilized with respect to time. As expected, the implanted side stabilized at a lower resistivity than that of the unimplanted side, indicating conductivity due to the implant. The temperature could then be dropped and a sequence of measurements as a function of temperature could be made.

Further work is planned with other implantations on high resistivity IIa samples using this technique to investigate the effect of other implants on the electrical transport characteristics in diamond.

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