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

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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. 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. Other applications where vide promise for new classes of high voltage optoelectronic devices is a significant engineering problem in supersonic cal properties of the wide

TABLE I. Selected properties of semiconductors

<table>
<thead>
<tr>
<th>Semiconductors</th>
<th>Band gap energy (eV)</th>
<th>Theoretical intrinsic limit (°C)</th>
<th>Melt temp (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ge</td>
<td>0.71</td>
<td>100</td>
<td>917</td>
</tr>
<tr>
<td>Si</td>
<td>1.12</td>
<td>300-350</td>
<td>1420</td>
</tr>
<tr>
<td>GaAs</td>
<td>1.43</td>
<td>450</td>
<td>1238</td>
</tr>
<tr>
<td>GaP</td>
<td>2.24</td>
<td>800</td>
<td>1470</td>
</tr>
<tr>
<td>AlGaAs</td>
<td>1.43-2.15</td>
<td>375-475</td>
<td></td>
</tr>
<tr>
<td>AlGaP</td>
<td>2.24-2.45</td>
<td>450</td>
<td></td>
</tr>
<tr>
<td>SiC</td>
<td>2.3-2.9</td>
<td>800-1200</td>
<td>a</td>
</tr>
<tr>
<td>Diamond</td>
<td>5.5</td>
<td>1100</td>
<td>b</td>
</tr>
<tr>
<td>BN</td>
<td>7.5</td>
<td></td>
<td>3000</td>
</tr>
</tbody>
</table>

* Sublimes above 1800 °C
* Transforms to graphite above 1200 °C

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.
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. 1

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 14,17 or silver paint contacts 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. 12 These contacts were reported to be non-ohmic and partially rectifying, but comparison to similar contacts formed on natural diamond. Point contacts to type Ib diamond were evaluated as a function of the metal work function of the metal and were found to be rectifying contacts over the temperature range of 25-300°C. The metals investigated in this study were In, Al, Ca, W, Xe, and Pr.

The transition metals have an affinity for carbon, and as suggested by Seal, 7 transition metal noble metal alloys in a 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 Raad 8 first used the approach suggested by Seal 9 to form thermistor elements from natural semiconducting diamond with a silver-copper-titanium alloy (60%, Ag, 25% Cu, 15% Ti). Collins et al. 10 used gold-tantalum (99% Au, 1% Ta) and gold-tantalum-aluminum (99% 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 11 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 compare quantitative 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/Pr/Au to natural diamond (type IIa) have been used as ohmic contacts in a study of high voltage optoelectronic switches. 11 In another study, 13 hard conducting diamond layers were produced by carbon implantation above a threshold dose of ~3 x 10^16 cm^-2. More recently, it has been reported 14 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, 14 boron ions were implanted (35 keV, 3 x 10^16 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 15 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. 15 This approach has also been utilized as a method of applying large area metal contacts to both natural and synthetic semiconducting diamond. 15 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. 16 More recently, an ArF laser was used to modify the surface of types IIa and IIb diamonds to a depth...
The laser-modified layers were stable ohmic contacts to type Ib 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 sp² (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.

III. 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, 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 allotrope 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 annealed 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, 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 chosen 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 0.15–0.2 µm thick grown on the dia-

![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.](image-url)
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 $1 \mu A$ at an applied potential of 10 V) as the as-received samples, illustrated in Fig. 5. Following the annealing step, a
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. 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.

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 liquidation 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. 6. Plot of current vs voltage for metallized contacts after annealing.](image)

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

![FIG. 8. Room temperature resistance as a function of annealing time at 950 °C for (C)/Mo/Ni/Au contacts for various pad spacings.](image)
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 CO-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 CO-Mo sample that had been annealed for 16 min at 950 °C. These studies indicate that the maximum 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. 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 Ka radiation, of the annealed (C)/Mo and of (C)/Mo/Au samples, with the gold film removed after annealing, produced a peak at 2θ = 37.8° and a much weaker peak at 2θ = 79.6°. These diffraction peaks are due to {111} and {222} planes of Mo₂C, respectively. The absence of other
VII. ADHESION 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 775°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 offset 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,C below 60 kbars,1,4 there can be no disagreement regarding the superior stability of molybdenum carbide, tantalum carbide, or titanium carbide relative to nickel carbide.3,4 Therefore, the relatively poor adherence of nickel to diamond compared to the adherence of molybdenum to diamond, etc. is not totally unexpected.

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

Mo$_2$C 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$_{0.58}$.
The reaction was characterized using AC 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 area 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.

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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).

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).
'I. A. Burgmaier, European Patent Application No. 89010595.8, date 28-10-89.