Correlation of the electrical properties of metal contacts on diamond films with the chemical nature of the metal-diamond interface. II. Titanium contacts: A carbide-forming metal

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The *I-V* characteristics of titanium contacts on polycrystalline diamond have been correlated with x-ray-photoelectron-spectroscopy (XPS) and Auger-electron-spectroscopy (AES) characterizations of the interface. As-deposited titanium contacts were rectifying in nature because of minimal interaction between as-deposited titanium and diamond as confirmed via XPS and AES. Once annealed, however, these contacts became Ohmic. The change was related to the formation of a carbide at the interface as observed by XPS. The Schottky-barrier height of the titanium contacts, which was determined by valence-band XPS, decreased from 1.3 to 0.8 eV as a result of the postdeposition annealing. It is believed that the carbide formation at the interface creates a diamond surface layer rich in electrically active defects which lower the barrier height of the metal and increase the leakage current. The interface between titanium and an argon-sputtered diamond surface was also characterized. Titanium formed as-deposited Ohmic contacts on the sputtered surface. A high density of ion-radiation-induced defects and a formation of a carbide during deposition both contributed to the Ohmic-contact formation. These contacts remained Ohmic after postdeposition annealing despite the fact that the annealing did not increase the carbide formed at the interface. It is believed that the carbide formed by the deposition of titanium behaved as a diffusion barrier to prevent the damaged layer from being annealed out into the titanium overlayer. It is concluded that most materials will yield rectifying contacts on a clean diamond surface. Ohmic contacts can be obtained by modifying the interface in some way (i.e., carbide formation, sputtering, etc.).

I. INTRODUCTION

As mentioned in the Introduction of paper I,[1] diamond is a useful material in which to fabricate electronic devices for specialized applications. As part of the effort to find suitable contacts to diamond, this study was intended to provide possible explanations of the electrical properties of metal constants and to establish selection rules for contact materials. As reviewed in paper I, reaction at the interface to produce a third phase is one of the useful methods to change the nature of metal contacts on semiconductors.[2,3] For diamond, the third phase is carbide which could be a reliable contact as well as a good diffusion barrier during high-temperature use.

Carbide-forming metals including titanium, molybdenum, and tantalum have been used to obtain Ohmic contact on diamond. Collins, Lightwowlers, and Williams used a gold tantalum alloy.[4] Titanium has been used by several groups of researchers and was often capped with gold overlayer.[5-9] After annealing at temperatures greater than 400 °C, good Ohmic contacts were obtained. Various combinations of carbide-forming refractory metals have also been studied to obtain Ohmic contacts of low resistivity.[5,6] Unique application of ion mixing to form graded junctions of Si/SiC diamond may be considered as a combination of carbide formation and damaging of the diamond lattice by Kr^+-ion implantation.[10] Bibliographic reviews of various methods of contact technology on diamond are found in Refs. 6 and 11. A variety of sample preparation, deposition conditions, and postdeposition treatments have been used so that it is difficult to compare those data in a quantitative manner. It is generally speculated that the Ohmic-contact formation is due to carbide formation at the interface enhanced by postdeposition high-temperature treatments. It should be noted here, however, that the diamond surface is easily graphitized in the presence of oxygen at high temperatures. This graphitization and interface reaction should not be confused. Either ultrahigh vacuum or an atomic hydrogen environment is required to prevent the development of a graphitic layer on the diamond surface during contact annealing.

Gold was studied to examine the effect of a non-carbide-forming metal in paper I. It was concluded that the absence of any interaction between gold and diamond led to the formation of rectifying contacts. In this paper, titanium was selected as a metal representing the carbide-forming metals for the following reasons. (1) Titanium is a transition metal which has a great affinity for carbon. Carbide formation is thermodynamically favorable ($\Delta H = -44$ kcal/mol at 25 °C). (2) It is estimated that the diffusion constant of carbon in titanium is orders of magnitude higher than those in the other carbide-forming metals.[12] Though titanium is the most widely used contact on diamond,[5-9] the actual mechanism for the Ohmic-contact formation has not yet been revealed.

The same format as paper I was adopted to characterize titanium contacts on polycrystalline diamond. Titani-

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um was deposited on diamond via thermal evaporation in ultrahigh vacuum. The deposition was interrupted several times to observe the development of the interface via x-ray photoelectron spectroscopy (XPS) and Auger-electron spectroscopy (AES). The effects of postdeposition annealing as well as predeposition argon sputtering of the diamond surface were also investigated. These results were compared with the *I-V* characteristics of the titanium contacts on diamond.

II. EXPERIMENT

The boron-doped polycrystalline diamond films were grown on silicon substrates in an identical manner to those used for the study of paper I. It was necessary to remove the impurities such as hydrocarbons and oxygen from the surface since titanium is so reactive that the gettering of such impurities could interfere with the interaction between pure titanium and diamond. Thus all the diamond samples were cleaned in a 3:4:1 solution of sulfuric, nitric, and perchloric acids heated to $\sim 80\,^{\circ}\mathrm{C}$ to remove the nondiamond carbons just prior to the introduction of samples into the vacuum system. Subsequently, the samples were heated to $\sim 500\,^{\circ}\mathrm{C}$ in vacuum to desorb as much of the physisorbed species as possible. Although this procedure provided the cleanest possible surface, a trace of oxygen was detected by XPS and AES and submonolayer fractions of hydrocarbons probably still remained.

Titanium was deposited by resistive heating of a titanium (99.99% purity) rod which was set ~ 10 cm from the sample surface and had previously been carefully degased. The typical deposition rate was 0.4 Å/min. The system was kept $\sim 1\times 10^{-8}$ Torr during the deposition. As in paper I, the equivalent thicknesses of deposits were determined using the two-dimensional overlayer model[13] for the intensity ratio of the Ti $2p_{3/2}$ peak from the overlayer to the Si $2p$ peak from a silicon substrate placed next to the diamond samples. The sensitivity factor ratio of the Ti $2p_{3/2}$ peak to the Si $2p$ peak was 7.6 for the system utilized in the present research.

The experimental procedures, the system for XPS and AES data acquisition, the postdeposition annealing, and the predeposition argon sputtering were identical to those described in paper I. The *I-V* measurements were also conducted in a similar manner. However, the titanium contacts were defined to the same contact-field configuration using the lift-off technique instead of etching the titanium.

III. RESULTS AND DISCUSSION

All the diamond films were observed under a scanning electron microscope (SEM) to confirm that there were no pinholes which would affect the results of XPS, AES, and *I-V* measurements. After several titanium-deposition intervals, the overlayer morphology was examined via SEM. Unlike the case of gold, cluster formation was not observed in any stages of titanium deposition on either silicon or polycrystalline diamond within the resolution of SEM. It was still not possible to assume a complete two-dimensional coverage so equivalent thicknesses in Å are used to indicate the overlayer thickness in the following discussion.

A. Electrical properties

The *I-V* characteristics of titanium contacts on boron-doped polycrystalline diamond are shown in Fig. 1. As-deposited contacts were rectifying, with a leakage current of only 1.2 μA at a reverse bias of 100 V. The leakage current was increased significantly by postdeposition annealing, and the *I-V* curve was essentially linear (i.e., Ohmic) after annealing at $430\,^{\circ}\mathrm{C}$. (The degree of linearity of the *I-V* curve of annealed titanium contact was not as good as those obtained by other researchers. The authors believe it will improve by annealing at higher temperature. The maximum annealing temperature of $430\,^{\circ}\mathrm{C}$ was chosen due to a limit of sample holder-heater configuration in the vacuum system.) The linear *I-V* characteristics of the annealed titanium contacts on diamond agree with previous results.[5-9] The interface characteristics were investigated using XPS and AES to provide possible explanations for these *I-V* characteristics.

B. Interface analyses of titanium coverage series

Titanium deposition on boron-doped polycrystalline diamond was interrupted several times to examine the development of the interface characteristics via XPS and AES. XPS C 1*s* peaks from diamond with various titanium coverages are shown in Fig. 2(a). The binding energy of the C 1*s* diamond peak was set at 284.6 eV to correct for charging of the sample. It was not necessary to consider the peak shape change due to a carbon-titanium impurity signal since it does not overlap with the C 1*s* peak from the diamond. The intensity of the C 1*s* peak was attenuated as the titanium overlayer thickness increased as illustrated by the poor signal-to-noise ratio at higher coverages in Fig. 2(a). The peaks illustrated in Fig. 2(a) were normalized to the same height for comparison. It has been reported[14,15] that the chemical shift (ΔE) of the C 1*s* peak due to the formation of titanium carbide is 2.7–3.3 eV. No such peak was observed during the de-

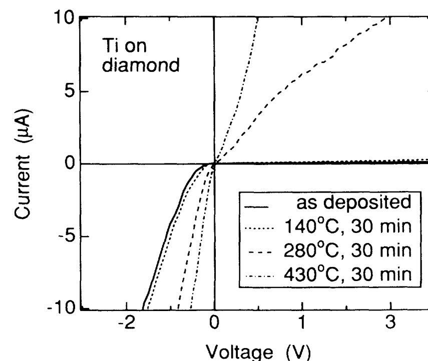

FIG. 1. *I-V* characteristics of titanium contacts on boron-doped polycrystalline diamond on silicon.

velopment of the titanium-diamond interface until a small hump appeared when 15 Å of titanium was deposited. As the thickness of the titanium overlayer increases, less and less of the diamond film is sampled (i.e., the intensity profile of electrons escaping from the sample drops exponentially from the surface and the diamond is effectively moving farther from the surface as titanium is deposited). As a result, the C 1*s* peak becomes much more sensitive to the carbon at the interface as well as to carbon in the titanium overlayer (if it is detectable by XPS). Since carbon contamination in titanium deposited on a carbon-free substrate was not detected by XPS, the small peak at 281.8 eV is believed to be the signal from carbide formed at the interface when the titanium was deposited.

The development of the Ti 2*p* peaks, which consist of a spin doublet, Ti $2p_{1/2}$ and Ti $2p_{3/2}$, at each deposition interval is illustrated in Fig. 2(b). The heights of the peaks are not normalized in this figure and illustrate the increased titanium concentration as deposition proceeds.

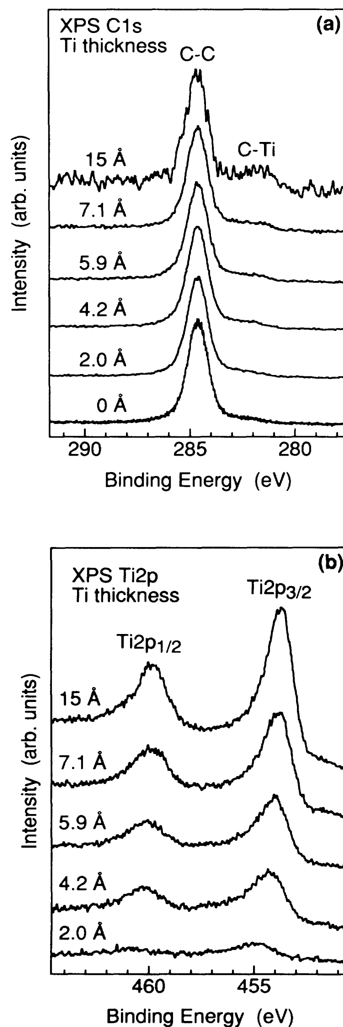

FIG. 2. (a) and (b) XPS spectra from boron-doped polycrystalline diamond at various titanium coverages; (a) C 1*s* and (b) Ti 2*p*.

The peaks shifted from high to low binding energy as the overlayer thickness increased. There are two possible reasons for this shift of peaks. If as-deposited titanium formed a carbide at the interface with diamond, at low overlayer coverage the Ti 2*p* peaks would be at the position of carbide which is 1.0–1.3-eV higher (for Ti $2p_{3/2}$ peak) than that of pure titanium.[14,15] As the coverage increases, the Ti 2*p* peaks are dominated by the signal of pure titanium and the peaks shift to lower binding energy. The other possible explanation for this energy shift is a cluster size effect (i.e., the shielding of core-level electrons by outer electrons is not as significant for a metal in small clusters as for that in the bulk and therefore more energy is necessary to extract the electrons from the core levels. Thus, the core-level peaks of the metal overlayer shift from high to low binding energy as the metal changes from a cluster to a bulk film).[16] It was not possible to choose one reason and to exclude the other. We believe the shift is due to both reasons but cannot determine, as yet, the dominant effect.

The XPS spectra thus indicate the presence of a thin layer of carbide at the interface between the diamond and the as-deposited titanium. The C_{KLL} Auger peak shape was also analyzed to probe the interface. It was found that the fine structure of the diamond did change to that of carbide upon titanium deposition for coverages greater than 4.2 Å. It is believed that the carbide was formed at the very surface of the diamond with the as-deposited titanium.

The Schottky-barrier height of the titanium on the diamond film was 1.3 eV. This value was calculated as the difference between the valence-band maximum of the diamond and the Fermi edge of the titanium overlayer. There are, to date, no reported values of the Schottky-barrier height for titanium contacts on diamond with which to compare this. However, this value of Schottky-barrier height is close to those for gold (1.1–1.7 eV), aluminum (1.1–1.5 eV), and tungsten (1.2 eV) determined for single-crystalline diamond[8,17,18] as well as for polycrystalline films.[19] This may suggest that the Fermi level is still pinned at the surface of the diamond film even with the presence of the very thin carbide at the interface.

C. The effect of postdeposition annealing

As discussed previously, postdeposition annealing was conducted *in vacuo* for 30 min at 140, 280, and 430 °C as indicated in Fig. 1. The transition of the *I*-*V* characteristics from rectifying to Ohmic corresponded to significant changes in the XPS spectra. The C 1*s* and Ti 2*p* peaks observed after annealing at various temperatures are illustrated in Figs. 3(a) and 3(b), respectively. A new C 1*s* peak at 281.8 eV became significant as the annealing temperature increased. The growth of this peak indicates an increase in carbon-titanium bonding. The binding energy of the Ti $2p_{3/2}$ peak also shifted from 453.7 to 454.7 eV. The energy shifts (i.e., difference) of 2.8 eV for the C 1*s* peak and 1.0 eV for the Ti $2p_{3/2}$ peak are in good agreement with the reported values[14,15] ($\Delta E_{\mathrm{C}\ 1s}$=2.7–3.3 eV and $\Delta E_{\mathrm{Ti}\ 2p_{3/2}}$=1.0–1.3 eV) of titanium carbide. The

characteristic valence-band spectrum of titanium carbide[20,21] was also observed after the 430 °C annealing. The Schottky-barrier height, calculated again as the difference between the valence-band maximum of the diamond and the Fermi edge of the titanium carbide, decreased to 0.8 eV after annealing at 430 °C. It should be noted that the most significant changes were observed after annealing at 430 °C in both core-level and valence-band spectra. This also agrees with the results of the *I-V* measurements. These core-level and valence-band spectra changes were not observed for titanium deposited on a carbon-free substrate and then annealed in the same manner. Thus, it was confirmed that the development of carbide was not due to the gettering of carbon contamination from the vacuum system.

Considering the dissociation energy of the carbon-carbon bond in diamond and the carbon-titanium bond in titanium carbide, one may question the formation of titanium carbide at the titanium-diamond interface by solid-state reaction at 430 °C. However, it should be noted that the bond-energy values available are valid for the bulk material but not necessarily for surface properties. It may be possible for a localized entropy effect to be dominant at the interface.

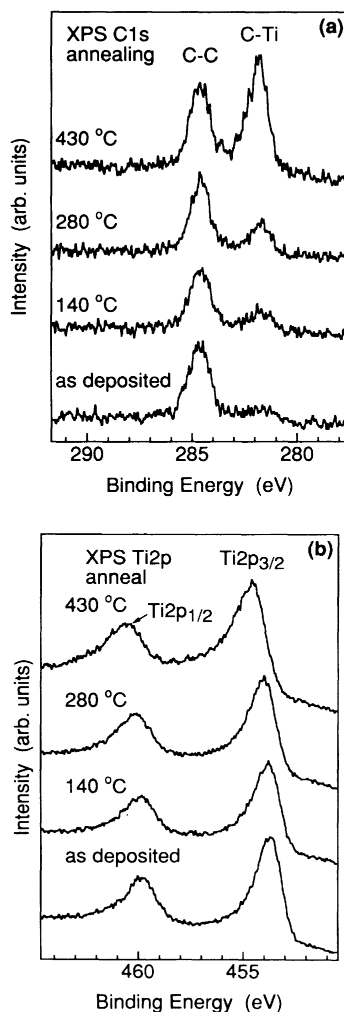

FIG. 3. (a) and (b) XPS spectra from boron-doped polycrystalline diamond after annealing at various temperatures; (a) C 1*s* and (b) Ti 2*p*.

D. The effect of predeposition argon sputtering

The effect of predeposition argon sputtering of the diamond surface was also examined. Argon sputtering creates a damaged surface which includes graphite and amorphous carbon.[22–26] The presence of this layer allowed as-deposited gold to form an Ohmic contact as seen in paper I. However, the Ohmic contacts became rectifying upon annealing. This change in the *I-V* characteristics was attributed to the instability of the damaged layer and the lack of interaction between gold and carbon (i.e., the damaged layer was absorbed by the gold overlayer because of the absence of chemical interaction). Therefore it was not a suitable condition for obtaining Ohmic gold contacts to polycrystalline diamond. However, it is still of interest to examine the influence of this damaged layer on titanium contacts because both the damaged layer and the carbide formation at the interface contribute to the formulation of Ohmic contacts.

A thick titanium layer (~2000 Å) was deposited on the argon-sputtered diamond surface. The contact-field pattern was obtained by the lift-off technique. The *I-V* measurements were conducted on the as-deposited as well as the annealed contacts and the results are illustrated in Fig. 4. The as-deposited contacts were Ohmic in contrast to those on nonsputtered diamond. It is believed that this behavior is due to the degeneracy of the damaged diamond surface. Thus, any metal would form Ohmic contacts on this type of sputtered surface. When these contacts were annealed, they remained Ohmic and the resistivity decreased slightly, suggesting the development of a path for more leakage current. This result is different from what was observed for gold contacts on an argon-sputtered surface which became rectifying after being annealed in the same manner. If the same change had occurred at the interface between titanium and the sputtered diamond by annealing (i.e., if the damaged layer had diffused into the overlayer), the *I-V* characteristics should also have returned to rectifying in this case. The

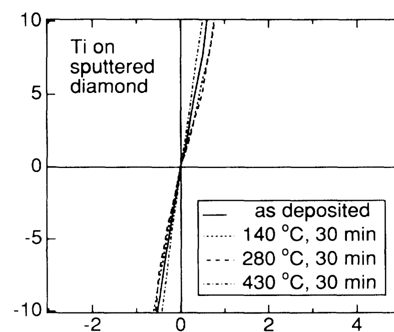

FIG. 4. *I-V* characteristics of titanium contacts on an argon-sputtered surface of boron-doped polycrystalline diamond.

following surface analyses were conducted to determine the details of this difference.

The XPS C 1*s* and Ti 2*p* peaks of the sputtered polycrystalline diamond at various thicknesses of titanium overlayer are shown in Figs. 5(a) and 5(b), respectively. The C 1*s* peak was set at 284.6 eV and used again to correct for sample charging. The peak broadening caused by the sputtering reflects the wider distribution of the core-level energies due to the various carbon-carbon bond distances and angles.[27] The development of the C 1*s* peak at 281.8 eV which indicates carbon-titanium bond formation was more significant during the process of titanium overlayer growth as compared to the nonsputtered diamond. The Ti 2*p* peaks at various stages of deposition showed even more significant differences from the case of the nonsputtered surface. The Ti $2p_{3/2}$ peak started at the binding energy of 454.7 eV and stayed at the position of titanium carbide until it moved toward that of pure titanium after the final titanium deposition. It did not show any overlayer cluster size effect. Thus

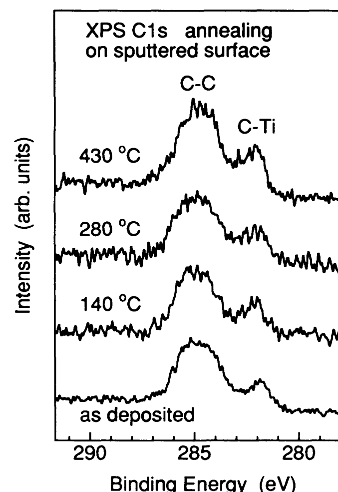

FIG. 6. XPS C 1*s* spectra from argon-sputtered polycrystalline diamond after annealing at various temperatures.

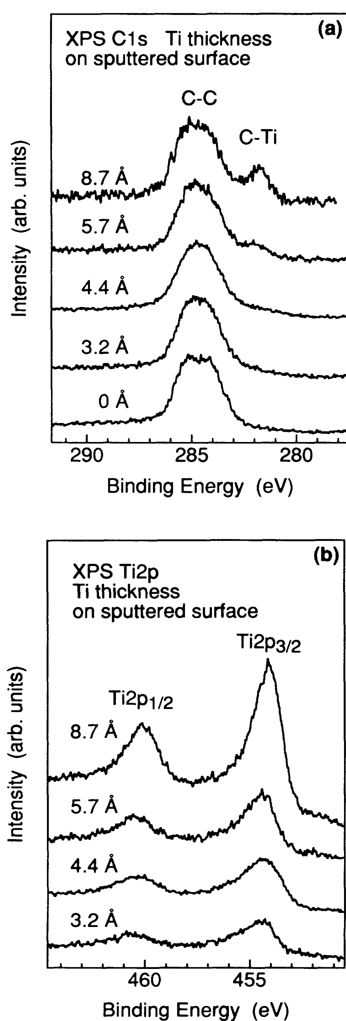

FIG. 5. (a) and (b) XPS spectra from argon-sputtered polycrystalline diamond at various titanium coverages; (a) C 1*s* and (b) Ti 2*p*.

both of the core-level spectra showed stronger interaction between the sputtered diamond surface and the as-deposited titanium. It is speculated that this was caused by the increased (i.e., metastable) energy state of the sputter-damaged diamond surface. Since the enthalpy of carbide formation is very negative even at room temperature, the activation energy is playing an important role in the carbide-forming reaction. This increased energy state is believed to help overcome this activation energy associated with the carbide formation. It is also noted that a defective diamond surface will also promote more diffusion of both carbon and titanium.

The effect of annealing the argon-sputtered diamond surface and the titanium overlayer was also examined via XPS. The XPS C 1*s* peaks after the annealing at various temperatures are shown in Fig. 6. The C 1*s* peak at 281.8 eV which reflects the titanium-carbon bonding did not grow significantly even after the annealing temperature was increased. The Ti 2*p* peaks (not shown) shifted from the position of pure titanium to that of carbide after 140 °C annealing and remained there. These results indicate that the carbide formation started upon the deposition of the titanium overlayer and was complete by 140 °C annealing. Further postdeposition annealing up to 430 °C did not cause the formation of additional titanium carbide. This is believed to be caused by the carbide, once formed, acting as a diffusion barrier against both carbon and titanium. Thus, annealing does not increase the concentration of electrically active defects at the diamond-titanium interface. However, the carbide formed before and/or during the early stages of annealing also prevents the defects already present at the diamond surface from diffusing into the titanium. As a result, the contacts remained Ohmic.

E. Discussion of interface band structure

A basic model of interface band structure is summarized in Fig. 7. It is believed that the interface between

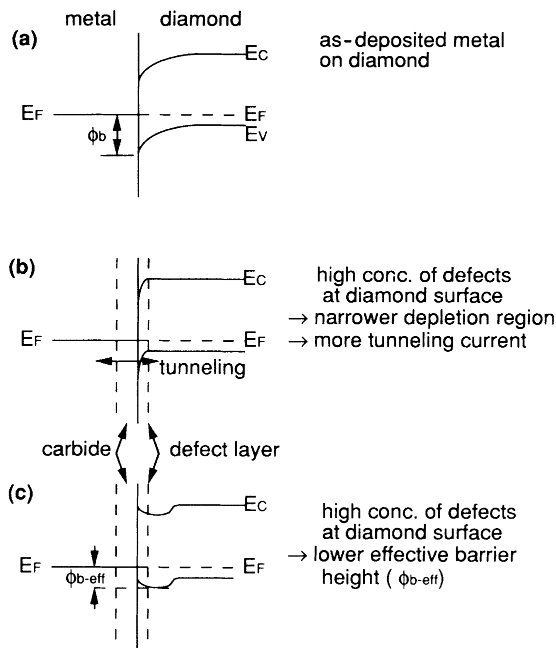

FIG. 7. Interface band diagrams of titanium on diamond; (a) as-deposited titanium on diamond, (b) high concentration of electrically active defects, which are created via the formation of a carbide and/or ion bombardment, reduces the depletion width and increases the tunneling current, (c) the electrically active defects created as in (b) decrease the effective barrier height.

the as-deposited metal and the diamond is similar to the one shown in Fig. 7(a). Considering work functions (ϕ) of the materials,[28] it is unlikely that titanium carbide forms an Ohmic contact while titanium and gold form rectifying contacts on *p*-type diamond (i.e., $\phi_{\text{TiC}} < \phi_{\text{Ti}} < \phi_{\text{Au}} < \phi_{B\text{-doped diamond}}$, thus one would expect the titanium carbide to be the best rectifying contact if work-function considerations were important). Rather, the Ohmic behavior of the annealed titanium contacts is attributed to defect formation at and near the diamond surface via the carbide-forming reaction. Such defects can either narrow the depletion width and increase the probability of tunneling as illustrated in Fig. 7(b), or decrease the effective barrier height as illustrated in Fig. 7(c). The contact resistance measured using a transmission line model (TLM) pattern for our titanium contact on diamond decreased with up to 5 h of annealing at 430 °C and increased for longer annealing times. Similar results have been reported for titanium by Narducci and co-workers[9] (an optimum annealing time of 1 h at 500 °C was observed) and for molybdenum by Moazed, Zeidler, and Taylor[6] (optimum annealing times of 4–8 min at 950 °C were observed). These results support this defect model [i.e., the defects out-diffuse by excessive annealing and the metal-diamond interface moves from the state shown in Figs. 7(b) and 7(c) to that in 7(a)]. It should be noted that the carbide-formation defect model is valid even if the Fermi level is pinned. (This is likely to be the case with diamonds as evidenced by the similar barrier heights of various metal contacts.[8,17–19]) Modification of interface structure and liberation of the Fermi level can cause the *I-V* characteristics to change from rectifying to Ohmic.

The as-deposited titanium contact on the nonsputtered diamond was rectifying even though it formed a trace amount of carbide as described in Sec. III B. This interface carbide layer is believed to be so thin that the titanium-diamond interface can still be considered nearly abrupt and the interface band structure is probably not modified significantly.

It is believed that the band structure at the interface between the metals and the argon-sputtered diamond surface is also similar to those illustrated in Figs. 7(b) and 7(c). The as-deposited contacts were Ohmic on the sputtered surface due to the sputter-induced defects at the interface. The Ohmic gold contacts on the sputtered diamond discussed in paper I lost this defect-rich layer by annealing and as a result reverted to rectifying contacts [Fig. 7(a)]. In the case of titanium, the titanium carbide that formed during deposition and/or the earlier stages of annealing limited the diffusion of these defects. As a result, the titanium contact on the sputtered diamond surface retained its Ohmic character even after the annealing.

IV. CONCLUSIONS

As-deposited titanium formed rectifying contacts on polycrystalline diamond. This was attributed to the minimal interaction of titanium with diamond, as determined from interfacial observations via XPS and AES. Once annealed, however, the rectifying contacts became Ohmic. This change was explained by the increase of carbide at the interface as observed by XPS. The titanium carbide formation which increases the electrically active defect concentration at the interface is believed to cause the Ohmic behavior of the annealed titanium contacts on diamond. The Schottky-barrier height decreased from 1.3 to 0.8 eV by annealing at 430 °C.

Predeposition argon sputtering produced a damaged layer at the surface of the diamond. XPS spectra indicated stronger interaction between as-deposited titanium and the damaged surface of diamond than in the case of a nonsputtered diamond surface. Again, the high concentration of electrically active defects at the diamond surface are believed to be responsible for the Ohmic behavior of the titanium contacts. Considering the change from Ohmic to rectifying that occurred for gold contacts on the sputtered surface of diamond (see paper I), the carbide formation at the interface is believed to prevent the contacts from returning to rectifying.

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[28]The work function of the polycrystalline diamond used in the present study is unknown. However, it is assumed that the Fermi level lies ~ 0.4 eV above the valence-band maximum (the activation energy of boron is 0.37 eV) and that the polycrystalline diamond has a positive electron affinity (i.e., the vacuum level is above the conduction-band minmum). The latter assumption is reasonable because diamond shows a negative electron affinity only for a clean (111) surface. Then, the work function of the diamond, which is equal to the sum of the electron affinity plus the difference between the conduction-band minimum and the Fermi level, is estimated to be 5.1 eV or larger, using a band gap of 5.5 eV. The work functions of gold and titanium are 5.1 and 4.3 eV, respectively. For titanium carbide, it is estimated to be ~ 2.6 eV from an experimentally measured value for monocrystalline titanium carbide [K. Senzaki and Y. Kumashiro, Bull. Electrotech. Lab. Jpn. **41**, 593 (1977)].