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Effect of surface hydrogen on metal-diamond interface properties

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Schottky barrier formation of metal contacts deposited on diamond (111) and (100) surfaces was investigated. Three different metals (Au, Al, and Ti) were studied because of their different chemical reactivity with C, i.e., Au being a nonreactive metal, Al a weak carbide-forming metal, and Ti a strong carbide former. Both fully H-terminated, unreconstructed (1×1) surfaces and H-desorbed, reconstructed $(2 \times 2)/(2 \times 1)$ surfaces with higher density of surface states were examined. Surface structures were determined via low-energy electron diffraction, and the change of surface band bending (SBB) and the interface chemistry during the contact formation were monitored using x-ray photoelectron spectroscopy. On the reconstructed surfaces, the SBB was independent of metal thicknesses. This was attributed primarily to Fermi-level pinning by the high density of surface states on the reconstructed surfaces. On the other hand, the surface-state densities were much lower on the unreconstructed surfaces and thus the Fermi level was not as strongly pinned as that on the reconstructed surfaces. When the metal coverage became large (>0.5 monolayer) on these unreconstructed surfaces, the charge transferred from the metal contacts to the diamond, the Fermi level moved upward in the band gap and the SBB increased. However, even on the unreconstructed surfaces where the density of pinning states were low, the SBB for thick metal contacts did not correlate to metal properties such as work function and/or electronegativity. Regardless of the state of the diamond surfaces, it was also important to consider the interface chemistry (chemical reactivity of the metal on diamond) to understand the change of the SBB after annealing the metal contacts.

I. INTRODUCTION

Diamond is a superior wide-band-gap semiconducting material with a unique combination of properties such as high breakdown voltage, high thermal conductivity, small dielectric constant, and excellent radiation hardness. These properties make diamond appealing as an active electronic device material for high-power, high-temperature, and harsh environment applications.^{1,2} Thus, various methods to fabricate ohmic and/or Schottky contacts on semiconducting diamond have been studied.^{3–12} Several excellent reviews^{2,3,13,14} are available for those who are interested in recent progress in the area of metal contacts on diamond.

In the present ongoing study (including previous papers by the authors given in Refs. 15-18), attention is focused on the basic mechanism(s) of Schottky barrier formation at metal-diamond interfaces. It is fair to say that the mechanisms that determine Schottky barrier height (SBH) at metal-semiconductor interfaces are still not fully understood despite years of effort.¹⁹⁻²³ The Schottky-Mott model, which is based on the work-function difference between the metal and semiconductor, is not supported by experimental data.^{24,25} To explain this, Bardeen proposed the original concept of Fermi-level pinning by surface states on a semiconductor.²⁶ The unified defect model of Spicer et al.^{27,28} attributes the origin of these surface states to charged defects at the interface. An alternate cause of these states is the penetration of the tails of the contact metal wave functions into the semiconductor [metalinduced gap states (MIGS) model].^{29,30} The interface chemistry is also considered to be important^{31–33} since, for example, the presence of interface phase(s) having their own work function would affect the SBH (effective work-function model).³⁴ For various transition-metal silicides-Si interfaces, the heat of formation ΔH was successfully correlated to values of the SBH.³⁵

There are many possible factors that can play an important role in determining the SBH at metalsemiconductor interfaces. Such factors include work function and/or electronegativity of the metals, ionicity, and/ or band gap of the semiconductor, densities of surface (interface) states, and interface chemistry (such as the heat of condensation of the metal and the heat of reaction between the metal and semiconductor constituents). In fact, there may not be a single model that can explain all cases of Schottky barrier formation. It is not the purpose of the present study to propose a new model to explain every aspect of Schottky barrier formation at metalsemiconductor interfaces. Instead, it is intended as a detailed examination of those possible factors which play an important role in determining the SBH for metal contacts on diamond. In the present study, the densities of surface (interface) states were altered by the various preparations of diamond surfaces as described in Sec. III. The effect of interface chemistry was examined by comparing three different metals (Au, Al, and Ti). According to previous studies^{15–17} on chemical reactivity of metals on diamond, Au is a nonreactive metal, Al a weak carbide-forming metal, and Ti a strong carbide former. It is interesting to study the SBH of metal contacts on diamond because it is fully covalent yet a wide-band-gap semiconductor as has been previously pointed out.^{36–39} Diamond Schottky diodes are also of technological importance due to the unavailability of *n*-type diamond.^{40,41}

II. ATOMIC AND ELECTRONIC STRUCTURE OF DIAMOND SURFACES AND PRESENCE/ABSENCE OF HYDROGEN

A brief review of atomic and electronic structure of diamond surface is given here due to its vital importance to the present study. There are several excellent reviews on the $(111)^{37,38,42}$ and $(100)^{43}$ diamond surfaces for those interested.

A. Atomic structure of diamond (111) surface

An as-polished diamond (111) surface shows a (1×1) low-energy electron diffraction (LEED) pattern. The (1 $\times 1$) pattern of the polished (111) surface changes to a $(2\times 2)/(2\times 1)$ structure on heating in vacuum ~1000 °C. 44,45 The (1×1) structure is restored by exposing the $(2\times 2)/(2\times 1)$ surface to atomic H.⁴⁵ Thus, it has been surmised that the polished surface is terminated by H atoms derived from the polishing oil. Direct evidence of H termination of the (1×1) surface was subsequently reported by Pate *et al.*^{37,46-48} who observed that H⁺ was desorbed from a (1×1) surface during photon-stimulated ion desorption time-of-flight (PSID-TOF) experiments. H⁺ from the surface was also detected by Hamza and co-workers⁴² using temperature-programmed desorption (TPD) an electron-stimulated desorption time-of-flight (ESD-TOF) spectroscopy. They succeeded in observing the upright termination of a (111) diamond surface from the angular distribution of the desorbed H^+ .

For the reconstructed $(2\times2)/(2\times1)$ surface, the π bonded chain model was suggested by Pandey.⁴⁹ The top two layers of carbon atoms are rearranged to have a zigzag chain structure on the reconstructed surface. A nice schematic of surface atomic structure has also been shown in Ref. 42. This model has been supported by many other studies including total energy minimization calculations,^{50,51} medium-energy ion scattering spectroscopy,³⁸ which successfully proved the dimerization, and photoemission spectroscopy.^{52–54} On this surface, no or only a weak signal of H⁺ was detected by TPD, ESD,⁴³ and PSID.^{37,46,47,55}

B. Electronic structure of (111) surfaces

Ihm, Louie, and Cohen⁵⁶ calculated the electronic structure of an unrelaxed, unreconstructed (111) surface using a self-consistent pseudopotential method. They predicted a sharp half-filled band in the band gap. Unfortunately, they used the assumption that an ideal (111) surface is terminated by dangling bonds which is now believed to be incorrect as described in the previous section.^{37,42,46–48}

Subsequently, various methods such as photoemission spectroscopy, ^{37,46–48,54,55,57–59} electron-energy-loss spectros-

copy (EELS),^{37,39,48,60} and x-ray absorption⁶¹ were employed to detect both occupied and empty surface states. Neither occupied nor empty states were observed on an unreconstructed (1×1) surface which was terminated with H; however, on the reconstructed $(2 \times 2)/(2 \times 1)$ surface, both occupied and empty surface states appeared. Pate et al.⁴⁷ determined that the filled surface states are centered at 1.1 eV below the valence-band maximum (VBM). According to Kubiak and Kolasinski,⁵⁴ the empty states peak at 4.8 eV above the VBM. The formation of these surface states accompanying the reconstruction is expected to pin the Fermi level at higher position in the band gap than the unreconstructed surface. This is consistent to the conclusion by Pate et al. 47,55,58,59 that the loss of negative electron affinity upon the surface reconstruction is due to the increase the downward band bending.

C. Diamond (100) surface

Studies on the diamond surface have mostly concentrated on the (111) surfaces; less attention has been given to the (100) surfaces in the past. Pate showed using PSID that the (100) surface is also terminated by H.³⁷ As for the (111) surface, it was observed that the (1×1) LEED pattern of the polished surface transforms to a (2×1) structure upon heating the sample in vacuum ~ 1000 °C.⁴⁴ The most intensive work on the (100) surface was reported by Hamza and co-workers.⁴³ They used TPD and ESD-TOF to successfully observe H⁺ from the unreconstructed surface. Two distinct H⁺ distributions, fast and slow, were observed on the unreconstructed surface. On the reconstruction, on the other hand, the fast component disappeared while the slower feature remained. These observations made them conclude that the (2×1) surface was composed of dimer pairs of monohydride C atoms. This view was also shared by Tsuno et al. who observed asgrown (100) surfaces of homoepitaxial diamond using reflection high-energy electron diffraction (RHEED) and scanning tunneling microscopy (STM).⁶² It is not surprising for the as-grown homoepitaxial diamond to have a monohydride surface since steric hindrance of neighboring H atoms is significant in the case of the dihydride surface. From ultraviolet photoemission spectroscopy (UPS) observations, Hamza and co-workers⁴³ also revealed the presence of occupied surface states in the band gap on the reconstructed surface. They further speculated that the empty states, if created by the surface reconstruction, are above the band gap since such states were not observed on the reconstructed surface.

III. EXPERIMENT

It is important to prepare the diamond surface carefully since the surface condition critically influences the properties of the interface. For example, Bell and Leivo⁶³ suggested from their point contact work that rectification on the diamond surface was dominated by surface-state pinning. On the other hand, Mori, Kawarada, and Hiraki⁶⁴ observed that the current-voltage (*I-V*) characteristics of point contacts to diamond depend on the electronegativity of the metals. They also reported that diamond cleaning procedures significantly affect the electrical characteristics. A similar effect of surface pretreatment was observed by Grot *et al.*⁷ In the present study, the diamond samples were handled in an ultrahigh-vacuum (UHV) environment (base pressure of 1×10^{-10} Torr) throughout the experiments. The vacuum system has been previously described in detail.¹⁵ Briefly, the UHV chamber was equipped with reverse-view LEED optics to observe the atomic arrangements of the surfaces, a coiled W filament heater to anneal the samples *in vacuo*, and a metal evaporation source. The main chamber was equipped for x-ray photoelectron spectroscopy (XPS) using a Mac2 semidispersive-type electron energy analyzer⁶⁵ and an x-ray gun with dual Mg-Al anodes.

Two types of diamond surfaces, (111) and (100), were examined in the present study. Prior to metallization, the surfaces of type-IIa single crystals were rubbed in olive oil to produce the H-terminated (1×1) surfaces.⁴⁴ They were subsequently rinsed with acetone and ethanol prior to introduction into the vacuum system. Once in the vacuum system, the samples and the sample holder were degased at 500 °C in a vacuum of 10^{-8} Torr. This degas process was essential to avoid graphitizing the surfaces by creating an oxygen-free atmosphere during the subsequent highertemperature desorption. The samples were then heated to 800 °C as a final preparation of the fully H-terminated, unreconstructed surfaces or to 950-1000 °C to produce the reconstructed surfaces. For heating, a coiled W filament was placed in close proximity to the back side of the Mo holder on which the diamond samples were mounted. If necessary, to increase the temperature, the W filament which was electrically isolated from the vacuum system. was negatively biased and electrons emitted from the filament were accelerated into the Mo holder. Temperatures were measured by a disappearing-filament optical pyrometer (Leeds & Northrup Co.) focused on the sample surface through a quartz window. LEED was used to monitor the atomic structure of the single-crystal diamond surfaces. After the initial degasing at 500 °C, the LEED patterns were very sharp (1×1) for both (111) and (100) surfaces. The (1×1) LEED pattern was retained on the reconstructed surface after the vacuum anneal at 800 °C. The reconstructed $(2 \times 2)/(2 \times 1)$ structure appeared after heating the samples at 950-1000 °C, as previously observed by many researchers. As has been reviewed in the previous section, the density of both occupied and empty surface states is higher on the reconstructed surfaces than the unreconstructed surfaces. Therefore, the effect of surface (interface) states on the Schottky barrier formation at metaldiamond interfaces may be evaluated by comparing the two types of surfaces.

Three metals (Au, Al, Ti) were deposited *in vacuo* via thermal evaporation from carefully degased sources placed ~ 20 cm away from the diamond surfaces. The interface chemistry between diamond and these three metals were studied previously. The interface reactivity was correlated with the electrical properties of the metal contacts.¹⁵⁻¹⁷ It can be considered that on a diamond surface, Au is a non-



FIG. 1. Schematic band diagram of a metal-diamond interface which illustrates the procedures to determine the SBH of metal contacts.

reactive metal, Al a weak carbide-forming metal, and Ti a strong carbide former. Thus, these three metals were studied to examine the effect of interface chemistry to the Schottky barrier formation at metal-diamond interfaces.

The XPS peaks were used to monitor the change of the diamond surface band bending (SBB) (ΔE) as a function of metal coverage and in vacuo postdeposition annealing at 430 °C for 30 min. Use of XPS also provides chemical information of the surface and interface with minimum disruption of the samples under study. Since type-IIa insulating diamond samples were used, sample charging shifted the photoelectron peaks to higher binding energies. This made it impossible to set the Fermi level at zero binding energy to determine the actual SBH. However, it was still possible to exclude the charging effect and to monitor the change of the SBB using XPS core-level peaks as follows (see Fig. 1). In addition to peaks of diamond (and deposited metal), a small O 1s peak was always observed on the sample surfaces, presumably due to oxygen from the vacuum system. The oxygen was in contact to the diamond surface, but it was not reacted with the diamond surface at room temperature. Thus, the O ls peak is at a constant location relative to the Fermi level of the sample, independent of SBB. (This assumption is also based on the observation of the O 1s peak. Its shape did not depend on either metal thickness or postdeposition annealing.) On the other hand, the position of the C 1s peak from diamond surfaces relative to the Fermi level depends on SBB of the diamond. Since the sample charging shifts both the O 1s and C 1s peaks by the same energy, the energy difference between the O 1s and C 1s reflects the change of SBB. It is common in photoemission studies to use emission from a metal contact to locate the Fermi-level position of the system.⁶⁶ However, in the present study it was not possible to determine the emission from the metal Fermi surface due to the poor signal-to-noise ratio for valence-band spectra, especially for small metal coverages. For this reason the C 1s and O 1s peaks were used instead of the metal Fermi level as described above.



FIG. 2. The change of SBB (ΔE) as a function of Au overlayer thickness determined by the C 1s core-level shift on various diamond surfaces. Those after the anneal at 430 °C are also shown.

IV. RESULTS

A. Surface band bending

In Figs. 2-4, the ΔE for Au, Al, and Ti contacts on both (111) and (100) surfaces are plotted as a function of metal overlayer thickness by setting $\Delta E=0$ for clean (before metal deposition) surfaces. When (C 1s-O 1s) is larger (smaller) than that of the starting surfaces, ΔE is expressed as a positive (negative) value. Those after the anneal at 430 °C for 30 min are also shown in the figures. The results of the unreconstructed, fully H-terminated surfaces with a (1×1) LEED pattern are indicated by open data points, while solid data points indicate those of the reconstructed surfaces with a (2×1) LEED pattern.

On the unreconstructed, H-terminated surfaces, the SBB was essentially unchanged for coverages below ~ 0.5 monolayer (ML). However, significant changes were observed for metal coverages of ~ 0.5 ML or more [except in the case of the Al on (100) surface]. There are two possible explanations for the observed evolution of SBB. The essen-



FIG. 3. The change of SBB (ΔE) as a function of Al overlayer thickness determined by C 1s core-level shift on variuos diamond surfaces. Those after the anneal at 430 °C are also shown.



FIG. 4. The change of SBB (ΔE) as a function of Ti overlayer thickness determined by C 1s core-level shift on various diamond surfaces. Those after the anneal at 430 °C are also shown.

tially constant SBB for submonolayer metal coverages can be explained by adatom cluster formation.^{67,68} That is, despite the large surface energy of diamond, the metal atoms at low coverages are likely to bond among themselves because the diamond substrate does not provide localized por d orbitals with which the metal atoms can satisfy their chemical bonds and become stable. Therefore, they form small clusters which interact only weakly with the diamond and leave the interface electronic structure unchanged relative to the clean surface. As the metal coverages increased, truly bulklike-metal-diamond interfaces are formed, yielding larger SBB. An alternative explanation of the nearly constant SBB at low metal coverages can be attributed to Fermi-level pinning by the oxygen at the sample surface. It was estimated from the XPS peak intensity⁶⁹ that the oxygen present on the surface was ~ 0.1 ML. This is large enough to pin the Fermi level of a semiconductor.⁷⁰ Hence the diamond surfaces were dominated by the oxygen until enough evaporated metal was deposited to dominate the interface characteristics.

On the other hand, the SBB on the reconstructed surfaces did not change significantly throughout the series of any metal deposition. This is primarily attributed to the higher density of surface states on the reconstructed surfaces than the unreconstructed surfaces. The Fermi-level pinning by the surface states yields the essentially constant SBB throughout the series of depositions.

The SBB of nonreactive metals (Au and Al) increased after the anneal at 430 °C, whereas that of Ti, which is a reactive metal, remained constant or decreased slightly after the same heat treatments. It is believed that the movements are related to the interface chemistry. Therefore, these results are discussed further in Sec. V B after describing the results of the interface chemistry analysis below.

B. Interface chemistry

As has been previously reported, Ti reacted with diamond and formed TiC at the interface upon annealing at 430 °C. Carbide-forming reactions were not observed at



FIG. 5. The C 1s peak of (a) unreconstructed and (b) reconstructed (100) diamond surfaces with various Ti coverages and after the anneal at 430 °C for 30 min. The peak at the smaller binding energy (\sim 282 eV) indicating Ti—C bonds increased more after the anneal of the Ti on the reconstructed surface.

Au-diamond and Al-diamond interfaces in those studies.¹⁵⁻¹⁷ Furthermore, it is believed from the previous results that the diamond surfaces did not transform to other forms of pure carbon such as graphite or amorphous carbon during the series of metal depositions and/or the postdeposition annealing.

There were no significant differences between the unreconstructed and the reconstructed surfaces in terms of the chemical reactivity with the nonreactive metals (i.e., Au and Al). According to the previous study,¹⁷ Al does not form a carbide layer on an undamaged diamond surface, but reacts with an Ar^+ -sputtered surface. Thus, it is considered a weak reactive metal on diamond. The nonreactive interface between the Al and the reconstructed surfaces in the present study is believed to be due to the small geometric strain in the reconstructed surface. In other words, it is necessary to have a more severely damaged and open diamond structure than just the small geometric strain introduced during reconstruction for a weak carbide forming metal such as Al to react chemically at the interface.

For the reactive metal, Ti, the reconstructed surfaces [both H-free (111) and monohydride (100) surfaces] showed more carbide formation than the H-terminated, unreconstructed surfaces as compared in Fig. 5. The higher chemical reactivity of the interface between the Ti and the reconstructed diamonds might be attributed to the slightly smaller bond strength of this surface as compared to the unreconstructed surface [C-H: 4.3 eV for a (1×1) surface but 2.6 eV for a (2×1) surface].⁷¹ In other words, the smaller bond strength between the surface atoms on the reconstructed surfaces might facilitate (the initiation of) the carbide forming reaction.

V. DISCUSSION

A. Analysis of SBB evolution

As described in Sec. III, it was impossible in the present study to determine the position of the Fermi level because of the sample charging. This is the reason why the data in Figs. 2-4 are presented as the deviation of the SBB. measured by the chemical shift of the C 1s peak from the diamond from the starting surface rather than by the SBH. However, if it was possible to precisely assume the Fermilevel position, the SBH could have been calculated from the data in Figs. 2-4. In fact, such a calculation was attempted by assuming that the C ls peak of the starting diamond surface was located at binding energy of 284.6 eV referenced to the Fermi level. It was also possible to measure difference between the C 1s peak and the valence band maximum, $E_{C ls} - E_v$, for the starting surfaces. The SBH, which is the difference between the Fermi level E_f and the valence-band maximum E_v for a *p*-type semiconductor, was then calculated as $SBH = E_f - E_v = 284.6 - (E_{C_{1s}} - E_v)$. Such a calculation yielded SBH values of 2.2-3.2 eV.

Recognizing the assumption as well as the difference in samples and sample preparation, the present results are compared to previous measurements of SBH at metaldiamond interfaces as follows. The SBH of various metal contacts including Au and Al on B-doped, type-IIb diamond have been measured using various methods such as capacitance-voltage (C-V), I-V, internal photoemission, and photoelectron spectroscopy.⁷²⁻⁷⁵ The SBH of Au on B-doped single-crystal diamond was found to be 1.7 eV using C-V measurement.⁷² Mead and McGill⁷³ used C-V, I-V, and internal photoemission to measure the SBH of 1.7-2.2 eV for Au and Al contacts on a similar singlecrystal diamond. Himpsel and co-workers⁷⁴ measured SBHs of 1.3 and 1.5 eV for Au and Al, respectively, on p-type diamond using photoelectron spectroscopy with synchrotron radiation. Their procedure of determining the SBH was slightly different from that in the present study. The SBH of 1.1 eV was determined using internal photoemission for Au and Al contacts on a polycrystalline diamond.⁷⁵ An SBH of Ti was 1.0 eV according to a photoemission measurement.⁷⁶ Thus, the previously measured SBHs were in the range of 1.0-2.2 eV, which is about 1 eV lower than the present values of 2.2-3.2 eV. It is believed that his difference is due to (i) the uncertainty in the C 1s peak energy referenced to the Fermi level (this assumption neglects the SBB of the starting surfaces), (ii) the difference in the surface preparation between the present and previous studies, and (iii) non-negligible experimental error which can be seen in the scattered data points in Figs. 2-4. The limitations of the first assumption are apparent considering the previous observation of a finite difference in SBB between the unreconstructed and reconstructed surfaces. 37,47,55,59,77

Even though the attempt to determine the absolute values of SBH from the XPS was not successful, it is still important to study the evolution of SBB as a function of metal thickness and postdeposition annealing to understand the metal-diamond interfaces. As mentioned in Sec. IV A, it is speculated that the constant SBB of low metal coverages on the unreconstructed surfaces (smaller surface-state densities than the reconstructed surfaces) are attributed to the small initial metal clusters which do not interact with the diamond surface, leaving the interface electronic structure unchanged relative to the surface before the metal depositions. An alternative explanation for this essentially constant SBB is due to the Fermi-level pinning by submonolayer oxygen observed on the diamond surfaces. The SBB of relatively thick (>0.5 ML) metal coverages became larger than those of low coverages. Thus, on the unreconstructed surfaces, the Fermi level was not as strongly pinned as on the reconstructed surfaces (or the density of pinning states, if they existed, was not high enough to block out the effect of relatively large metal charges). No surface states (either occupied or empty) were experimentally observed on the unreconstructed surfaces.

The constant SBB throughout the series of metal deposition on the reconstructed surfaces are most likely explained by the Bardeen model in which the surface (interface) states pin the Fermi level. For the reconstructed (111) surface, Pandey⁴⁹ predicted the dimerized π -bonded chain model, which has been supported by many subsequent studies.^{38,52-54} The density of states originating from the reconstruction on these surfaces could be high due to the small lattice constant of diamond. The presence of surface states (both occupied and empty) on the reconstructed surfaces has been observed using various methods such as photoemission, ^{37,46–48,54,57–59,78} x-ray absorption,⁶¹ and EELS.^{37,39,48,60} These techniques, however, did not detect any surface states in the band gap on the unreconstructed surfaces as reviewed in Sec. II. The Fermi-level pinning by the high density of surface states is also consistent with a study by Pepper⁷⁹ who reported a larger static friction coefficient between Cu and a reconstructed diamond surface than the unreconstructed surface. The friction force was attributed to the interaction between the metal conduction-band electrons and the band-gap states on the reconstructed diamond surface. A similar result in terms of the relation between the low/high friction and the presence/absence of surface-terminating hydrogen was also observed on polycrystalline diamond.^{80,81}

An attempt to correlate the SBB of thick Au, Al, and Ti contacts to their work function and/or electronegativity (Pauling scale)⁸² relative to diamond was not successful. This does not agree with the previous observations by Mori and co-workers⁶⁴ who reported the dependency of metal electronegativity on the I-V characteristics (ohmic versus rectifying) of point contacts on B-doped polycrystalline chemical-vapor-deposition (CVD) diamond. Obviously, different experimental conditions contribute, at least partially, to the different observation. For example, their work used point contacts on B-doped polycrystalline diamond which was cleaned in a mixture of CrO₃ and H₂SO₄. On the other hand, in the present study metals were deposited on insulating single-crystal diamond in an UHV environment. In addition, the experimental error in ΔE values are substantial as seen in the scattered data points in Figs. 2-4 in the present study. Thus, the present results are inconclusive in terms of the correlation of the SBH to the metal properties (work function and/or electronegativity), and therefore, the contribution of the MIGS model at metaldiamond interfaces may not yet be excluded.

B. Correlation of SBB to the chemical reactivity of metal

The metal-diamond interface chemistry has previously been studied in detail using XPS and Auger electron spectroscopy (AES).¹⁵⁻¹⁷ Au contacts on polycrystalline diamond did not show any evidence of chemical reaction at the interface.¹⁵ On the other hand, Ti deposited on an asgrown diamond surface formed a carbide at the interface upon annealing at 430 °C.¹⁶ Ti on an Ar⁺-sputtered diamond surface reacted to form the carbide at even lower annealing temperature (140 °C). Al, which is thermodynamically a weak carbide former, did not react with an as-grown polycrystalline diamond after the annealing up to 430 °C, but did form a carbide on the Ar⁺-sputtered surface.¹⁷ It was found that a substantially damaged diamond surface and/or higher annealing temperatures are necessary for Al to react with diamond. The present observation of reactive Ti-diamond interfaces and nonreactive Au- and Al-diamond interfaces are consistent with those previous results for polycrystalline diamond. We suggest that it is necessary to have a more severely damaged and open diamond structure than just the small geometric strain introduced during the reconstruction for a weak carbideforming metal such as Al to react chemically at the interface.

It is important to consider the interface chemistry to understand the change of SBB after the anneal at 430 °C. As shown in Figs. 2 and 3, the SBB decreased after the anneal for nonreactive metals (Au and Al). A similar result which was observed as a decrease of the SBH of Al after annealing has been observed previously.^{74,77} It might be attributed to the agglomeration of metal clusters by the anneal, which in turn decreases the effect of the charge transfer from the metal. This speculation is based on the fact that the C 1s peak intensity increased after the anneal. On the other hand, the SBB of Ti, which is a reactive metal on diamond, decreased for the final thick deposition and stayed the same or increased slightly after the subsequent anneal as shown in Fig. 4. The initial decrease might be due to the agglomeration, similar to Au and Al, caused by heating from the evaporation source for an extended period of time. The subsequent increase of the SBB is explained by the formation of TiC at the interface. The small work function value of TiC is expected to form a higher Schottky barrier.

VI. CONCLUSIONS

The SBB was found to be independent of metal thickness on reconstructed diamond (111) and (100) surfaces. This was attributed primarily to the Fermi-level pinning by the high density of states present on such reconstructed surfaces. On the other hand, the density of such surface states was low or did not exist on the unreconstructed surfaces. The Schottky barrier was developed at the interface via charge transfer from the metal. It is also important to consider the interface chemistry to understand the SBB of the heat treated contacts. The SBB decreased after the anneal for nonreactive metals (Au and A1) due to the agglomeration of metal clusters by the anneal, which in turn decreased the effect of the charge transfer from the metal. The SBB of Ti, which is a reactive metal on diamond, decreased for the final thick deposition and stayed the same or increased slightly after the subsequent anneal, which was related to the formation of TiC at the interface.

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