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Effect of Electronic Structure of the Diamond Surface on the Strength of the Diamond-Metal Interface

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EFFECT OF ELECTRONIC STRUCTURE OF THE DIAMOND SURFACE

ON THE STRENGTH OF THE DIAMOND-METAL INTERFACE

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Abstract

Recent electron spectroscopic investigations have shown that the diamond surface undergoes a transformation in its electronic structure by a vacuum anneal at ~900° C. The polished surface has no electronic states in the band gap, whereas the annealed surface has both occupied and unoccupied states in the band gap. In addition, the annealed surface exhibits some electrical conductivity. The effect of this transformation on the strength of the diamond-metal interface is investigated by measuring the static friction force of an atomically clean metal sphere on a diamond flat in ultrahigh vacuum. The friction force is due to interfacial bonding. It is found that low friction (weak bonding) is associated with the diamond surface devoid of gap states whereas high friction (strong bonding) is associated with the diamond surface with gap states. Exposure of the annealed surface to excited

hydrogen also leads to weak bonding. The interfacial bond will be discussed in terms of interaction of the metal conduction band electrons with the band gap states on the diamond surface. Effects of surface electrical conductivity on the interfacial bond will also be considered.

Introduction

The electronic structure of the diamond surface has recently been observed to undergo a transformation by vacuum annealing at ~900° C. Prior to annealing the polished surface exhibits no surface states, whereas the annealed surface exhibits both occupied (ref. 1, 2) and unoccupied (ref. 3, 4) surface states. The annealed surface also exhibits some electrical conductivity (ref. 5). Since the electronic structure of a semiconductor-metal interface is determined by the electronic structure of the semiconductor surface with which the interface is formed (ref. 6), the diamond-metal Schottky barrier should be affected by this transformation. An understanding of Schottky barrier formation is important in solid state electronics and has been the subject of intense investigation in this journal.

A very different area in which the electronic structure of the diamond surface may be important is the metal working industry. The strength of the diamond-metal interface is a factor determining the wear of diamond cutting tools and the life of diamond-impregnated grinding wheels. Interfacial strength is affected by interfacial chemical bonds that may be formed and these bonds are part of the interfacial electronic structure. Thus the transformation of the electronic structure of the diamond surface is likely to affect the strength of the diamond-metal interface.

In this paper it is shown that there is a correlation between the electronic structure of the diamond surface as probed by electron energy loss spectroscopy (ELS) and the strength of the diamond-metal interface as probed by the static coefficient of friction of a metal sphere on a flat diamond in ultrahigh vacuum. We first review the evidence obtained by ELS for the appearance of unoccupied states in the band gap of the annealed diamond surface. The static friction experiment is then described and the correlation between the appearance of unoccupied gap states on diamond with high static friction is demonstrated. The results presented here are for the (110) surface of diamond, but similar results have been obtained for the (111) surface. Finally, the interfacial chemical bond is discussed in terms of elementary concepts of molecular orbital theory.

Diamond Surface

The understanding of the diamond surface has recently been furthered by electron spectroscopies. Photoemission spectroscopy has shown that the surface annealed at $\sim900°$ C exhibits occupied surface states near the top of the valence band and possibly in the band gap (ref. 1, 2). ELS probes unoccupied surface states and shows that the annealed surface exhibits unoccupied surface states that appear in the band gap (ref. 3). The electrical conductivity observed for the

annealed surface is evidently related to these surface states in the vicinity of the band gap. The use of ELS is particularly appropriate here because the interfacial chemical bond will be considered in terms of the interaction of metal electrons with unoccupied surface states on diamond.

Figure 1 presents the energy loss spectra for ionization of C(1S) electrons into empty states (ref. 3, 4). The damaging effect of the electron beam has been eliminated as reported (ref. 3). The large feature (labeled K_1) is due to a transition into the lowest maximum in the conduction band density of states. The top of the 5.5 eV band gap has been positioned at the bottom of the conduction band which was determined by taking the energy interval of 3.6eV between the lowest maximum (K_1) and the bottom of the conduction band from a band structure calculation (ref. 7). A polished diamond surface exhibits no states in the band gap. After annealing at ∿900° C, the spectrum exhibits an additional feature labeled K_0 located in the band gap. This is obseved for both the (110) and (111) surfaces. The magnitude of K_0 as a function of temperature for successive two minute annealing cycles is indicated for the (110) surface in Fig. 2. For this annealing schedule the transformation for the polished surface begins ∿850° C and is complete by ∿900° C.

As indicated in Fig. 1, the K_0 feature could be removed by exposing the annealed surface to hydrogen excited by the ionization gauge filament for 10 minutes at 5×10^{-5} torr (ref.

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4). When this "regenerated" surface is subjected to the above annealing schedule, the K_0 feature appears first at a lower temperature than for the polished surface. The large increase to the maximum value, however, occurs at the same temperature for both surfaces. There is thus a difference, not as yet understood, between the polished and regenerated surface even though they are both devoid of unoccupied surface states.

There are two points in these results that must be discussed. First, it is widely assumed that the polished surface is covered with a chemisorbed layer of nydrogen that is responsible for the absence of surface states (ref. 1, 2). Annealing ($\sim 900°$ C) or electron bombardment (ref. 3) presumably removes the hydrogen and generates the observed surface states. The removal of the unoccupied states by exposure to hydrogen can be taken as evidence for chemisorbtion of hydrogen. However, at this time there is still no direct experimental detection of surface hydrogen and this must still be treated as an assumption. Second, there is the question of whether the energy of the unoccupied surface state is in the band gap of the ground state of the crystal or whether it lies higher in the conduction band. The difference is due to the effect of electron-core hole binding energy (exciton) and has been encountered in the determination of the energy of surface states on GaAs, for example (ref. 8). The question must be resolved before a theory of the interfacial chemical bond based on gap states on diamond can be developed.

To summarize these results, the polished surface exhibits no unoccupied surface states and is probably covered with chemisorbed hydrogen. Annealing the surface to ∼900° C introduces unoccupied surface states in the band gap and removes the hydrogen. Exposure to excited hydrogen removes the unoccupied surface states, although this regenerated surface may not be the same as the polished surface.

Diamond - Copper Friction

The strength of the diamond-metal interface is assessed by the static friction of an atomically clean copper sphere on the flat diamond as a function of diamond surface condition. The basis for this approach is the adhesion theory of friction (ref. 9) according to which the tangential force is due to the rupture of interfacial adhesive bonds formed at asperity contacts. This approach to understanding interfacial strength has been used to investigate the Al_2O_3 - metal system (ref. 10). The trends observed in the static friction experiments have also been observed in thin film adhesion so that under these experimental conditions static friction is considered at least as a reliable probe of interfacial strength as is thin film adhesion.

The experimental apparatus has been described before (ref. 10) and consists of the copper sphere contacting the flat diamond at a pressure ∼5×10^{-9} torr in the same chamber used

for surface analysis. The diamond is subjected to the thermal treatment discussed above and the sphere is cleaned by argon ion bombardment after each anneal. The normal load of the sphere on the flat is 57 gmf. and the tangential force developed is sensed by a piezo-electric torce transducer on the diamond mount. This force is developed within a few micrometers of relative displacement of the sphere with respect to the flat after which the force no longer increases and the system starts to slide. In our experiments the static and kinetic friction forces were the same. This maximum friction force is expressed as a fraction of the normal force (coefficient of friction) and is used here simply to indicate the relative strength of the interface as a function of diamond surface condition, an increase in friction implying an increase in interfacial strength.

In Fig. 3 the coefficient of friction μ as a function of annealing temperature is presented. The value of μ for the polished surface annealed at $\sim750°$ C is about 0.11. Other experimental trials have yielded $\mu \sim 0.05$, outstandingly low values for an atomically clean solid interface. The friction is then observed to increase to ~0.5 after annealing the diamond at $\sim850°$ C, the same annealing temperature for which unoccupied surface states appeared in the energy loss spectrum (Fig. 2). Thus there is a correlation between increased interfacial strength and the appearance of unoccupied surface states in the band gap. This correlation was observed

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witn both the (111) and (110) surfaces. It was observed before the transformation of the surface electronic structure was known and in fact prompted the surface analysis that led to the observation of surface states (ref. 3). This lends confidence to the interpretation of the friction in terms of surface effects.

The increase in friction was also observed after bombarding the polished diamond surface with 500eV electrons. Since it has been shown that unoccupied gap states are generated by electron bombardment, this supports the above correlation.

After the friction attained the high value, the diamond was exposed to excited hydrogen, after which the copper sphere was recleaned. As indicated in Fig. 3, the friction was reduced, although not to the initial value of ~ 0.11. The reduction in friction is in accord with the above correlation since the unoccupied surface states are removed by hydrogen exposure. The fact that it does not return to its initial value may be related to the appearance of a small amplitude of K_0 at temperatures lower than that of the initial transformation. In any case the friction does again increase to its high value after annealing at the same temperature ($\sim 850^\circ$ C) for which the increase was first observed.

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Discussion

The correlation of high interfacial strength with the presence of unoccupied surface states in the band gap leads to consideration of a possible interfacial chemical bond based on the energy level diagram of Fig. 4. First, recall from elementary molecular-orbital theory of chemical bond formation that a bond is formed by partially occupied orbitals of similar energy (ref. 11). The orbitals that constitute the valence band of diamond are fully occupied, while the orbitals that constitute the conduction band are empty. Thus for the diamond surface, without gap states, the Fermi level electrons - those electrons with the highest energy in the metal - must interact with the (empty) conduction band orbitals in the diamond to form a chemical bond. It may be that the energy difference between the bottom of the conduction band and the Fermi level is too large to allow a bond to be formed and this may account for the low friction. On the other hand, the unoccupied states in the band gap of the annealed surface lie much closer in energy to the Fermi level and this smaller energy difference may allow a bond to be formed by the Fermi level metal electrons and the empty gap states. Such a bond would increase interfacial strength and lead to higher friction. Since electron bombardment of diamond generates unoccupied gap states, interfacial bonds should be possible after this treatment as well, leading to the observed higher friction.

Note that this chemical bonding explanation requires the energy of the unoccupied surface states to be in the band gap of the crystalline ground state. If in fact the energy lies in the conduction band (as discussed above), then the chemical bond is unlikely to be formed and a different explanation for the change in interfacial strength must be sought. For example, one might consider the occupied (ref. 1, 2) instead of the unoccupied surface states. It is these states that presumably lead to the observed electrical conductivity. It has been shown by Ferrante and Smith (ref. 12) that the interaction of the free electrons at a bimetallic interface leads to a strong adhesive bond. If the annealed surface is indeed metallic, then a strong bond with the metal might result. However such an explanation requires a determination of whether the surface is metallic or semiconducting, a matter that is still in question even for well studied silicon surfaces.

An understanding of the diamond-metal interfacial strength may be considered in the same light as the attempts to understand the Schottky barrier of the semiconductor-metal interface. Both interfacial strength and potential barrier are determined by interfacial electronic structure. Theories of the Schottky barrier have relied heavily on the understanding of the silicon surface, a field which is well developed. However, the investigation of the diamond surface is just beginning and much more definite information is required before a theory of interfacial strength can be realistically developed.

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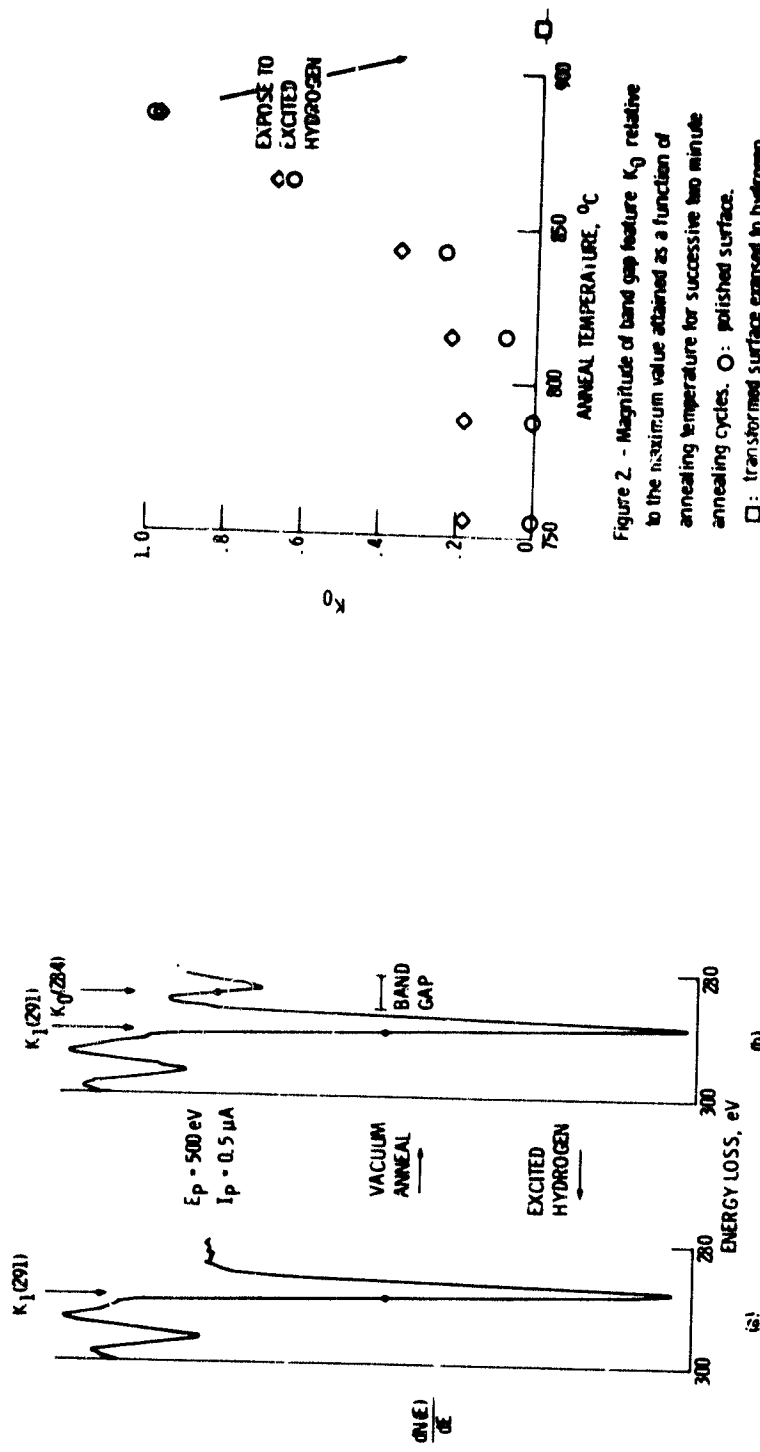12. J. Ferrante and J. R. Smith, Phys. Rev. B 19, 3911 (1979).

Figure 1. - Ionization loss spectra of diamond (110). In (a) the surface is either freshly polished or exposed to excited hydrogen. In (b) the diamond has been annealed $\sim 900^\circ$ C to develop K_0 to its maximum size of 0.14 K_1. The values of the energy loss depicted are taken at the arithmetic mean of the maximum and minimum in these derivative spectra.
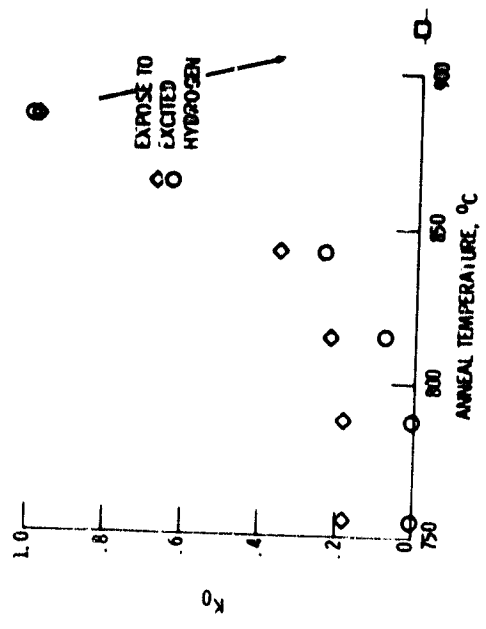
Figure 2. - Magnitude of band gap feature K_0 relative to the maximum value attained as a function of annealing temperature for successive two minute annealing cycles. O: polished surface. □: transformed surface exposed to hydrogen. ◇: transformed surface exposed to hydrogen and then annealed.

Figure 3. - Copper-diamond static friction coefficient as a function of diamond annealing temperature. O: polished surface. □: transformed surface exposed to excited hydrogen. ◇: transformed surface exposed to hydrogen and then annealed.

Figure 4. - Schematic representation of the density of states for the copper and diamond surface near the energy gap of diamond. The diamond has been depicted with both occupied and unoccupied surface states in the gap, which are absent on the as-polished surface.

EXPOSE TO EXCITED HYDROGEN

ANNEAL TEMPERATURE, °C

K_0

K_1 (291) K_0 (284)

E_p = 500 eV
I_p = 0.5 μA

$\frac{d[N(E)]}{dE}$

BAND GAP

VACUUM ANNEAL

EXCITED HYDROGEN

K_1 (291)

ENERGY LOSS, eV

(a)   (b)

Figure 1. - Ionization loss spectra of diamond (110). In (a) the surface is either freshly polished or exposed to excited hydrogen. In (b) the diamond has been annealed ~900°C to develop K_0 to its maximum size of 0.14 K_1. The values of the energy loss depicted are taken at the arithmetic mean of the maximum and minimum in these derivative spectra.

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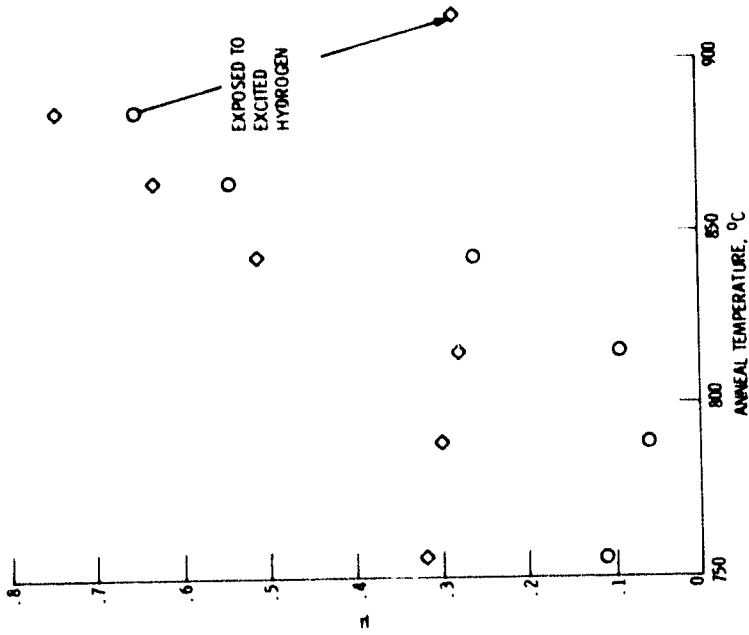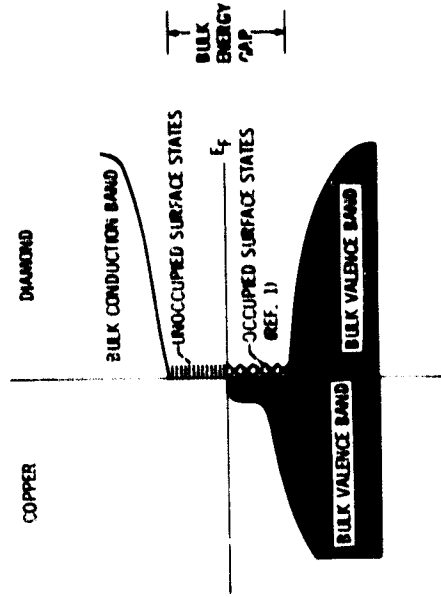

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