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Near-Ideal Schottky Barrier Formation at Metal-CVD Diamond Interfaces

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Schottky barrier heights between various metals and an H-terminated semiconductor have been measured quantitatively using homoepitaxial CVD diamond. The obtained ideality factor using Al point contacts to diamond is 1.01, which is the nearest value to unity ever reported in diamond. A strong correlation between the SBH and the electronegativities of metals is observed, and even the ohmic property is obtained when metals with higher electronegativities are used. According to this result, the Fermi level is scarcely pinned at the interface between metal and diamond.

1. INTRODUCTION

Schottky barrier heights (SBHs) of diodes utilizing CrO_3 treated surfaces have almost no dependence on the work function or the electronegativity of metal.[1,2] Although CrO_3 treatment is effective for removing graphite, oxygen was found to remain on the surfaces after the treatment.[3] Furthermore, the surface reconstruction on (001) surfaces due to hydrogen termination has been lost and the details of the treated surface have not been well studied. On the other hand, the existence of a p-type semiconductive layer on undoped CVD diamond as-deposited surfaces has been reported recently.[4,5] As-deposited CVD diamond surfaces are considered to be terminated by hydrogen,[6] and they have been investigated in detail using STM[7,8] due to conductivity of the film. In this respect, as-deposited (i.e., H-terminated) CVD diamond surfaces can be regarded as well defined.

Metal-dependent diodes were obtained using as-deposited CVD diamond polycrystalline film,[3,9] where the H-terminated surface still remains at the interface even after deposition of metal. However, quantitative measurement of SBH has not been performed due to the presence of its grain boundaries. In this investigation, we will quantitatively discuss the dependence of SBHs on the various metals with as-deposited CVD diamond homoepitaxial films.

2. EXPERIMENTAL

Homoepitaxial undoped diamond films was prepared on synthetic Ib diamond (001) substrates (1.5x2.0x0.3 mm) by microwave plasma-assisted CVD. Reaction gases were CO or CH_4 diluted with H_2(5 or 10%). Fourteen kinds of metal wires (0.5mm diameter) were used as point contacts. Five kinds of metal dots (0.3 mm diameter) were fabricated on the homoepitaxial diamond films by the vacuum evaporation method. Metals were evaporated at room temperature. Ag paste functioned as an ohmic contact on the coplaner side of the diamond surface conductive layer. A Hewlett Packard model 4140B pA meter and voltage source were used to record the I-V characteristics. All I-V measurements were automated with a personal computer.

3. RESULTS AND DISCUSSION

The I-V characteristic of an Al point contact with a homoepitaxial diamond film formed by CO (10 %) diluted with H_2, is shown in Fig.1. The Schottky characteristic is linear over 5 orders of magnitude on the semilogarithmic plot. The ideality factor is 1.01, which is the nearest value to unity ever reported in diamond. This implies that quantitative measurements of the SBH can be performed in the homoepitaxial diamond films. The obtained SBH is 0.83 eV, which was calculated with the contact area given as $10^{-5}cm^2$. The estimation of the contact area is mainly confirmed by comparison with the reverse characteristic of an evaporated contact.

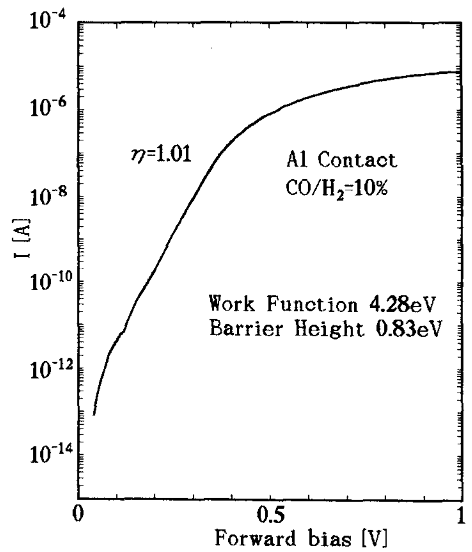

Fig. 1. I-V characteristics of an Al point contact to an as-deposited CVD diamond homoepitaxial film.

Differences in I-V characteristics and SBHs between several metals used for contacts were investigated. The n factors of point contact diodes utilizing Pb and Zn are 1.04 and 1.13, respectively, which implies that both characteristics are comparable to those of Al point contacts. The averaged n factors, SBHs and rectification ratios of each metal contact are listed according to the electronegativities of metals in Table 1. It indicates the tendency of the SBH to decrease as the electronegativities of metals increase.

I-V characteristics of evaporated metal dot contacts (0.3 mm diameter) to CVD diamonds were also measured. The Schottky property was obtained when metals such as Mg, Al, Pb and Zn were used for the electrode. Such metals are reported to be nonreactive with carbon. The n factors and the rectification ratios are worse than those of the point contact. One of the reason is that the larger contact area includes the more recombination sites deteriorating ideality factors. The SBHs with respect to the electronegativities of the metals are shown in Fig. 2. It indicates a strong correlation between the SBHs and the electronegativities of the metals.

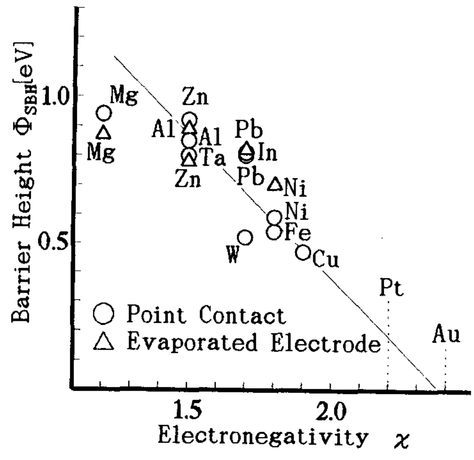

Fig. 2. SBHs with respect to the electronegativities of the metals. Circular plots indicate point-contacted electrodes, and triangles indicate evaporated ones.

On the other hand, ohmic properties were obtained when metals with high electronegativity, such

Table 1. Differences in ideality factors,SBHs and rectification ratios with respect to the electronegativities of metals. These are average values of more than ten point of each samples.

Metals	Electronegativities x	Ideality factor n	Schottky barrier height Φb[eV]	Rectification ratio
Mg	1.2	1.4	0.94	10^8
Zn	1.5	1.2	0.92	10^7
Al	1.5	1.3	0.85	10^7
Ta	1.5	1.4	0.80	10^6
In	1.7	1.4	0.81	10^6
Pb	1.7	1.1	0.80	10^6
W	1.7	2~4	0.52	10^2
Ni	1.8	1.2	0.58	10^4
Fe	1.8	1.6	0.54	10^3
Cu	1.9	3~6	0.47	10^1

as Pt, Au, Pd and Ag, were used. The ohmic property of an Au point contact to CVD diamond is shown in Fig. 3. The linear property shown in Fig. 3 was unchanged when the range of voltage become wider (-20 to +20 V).

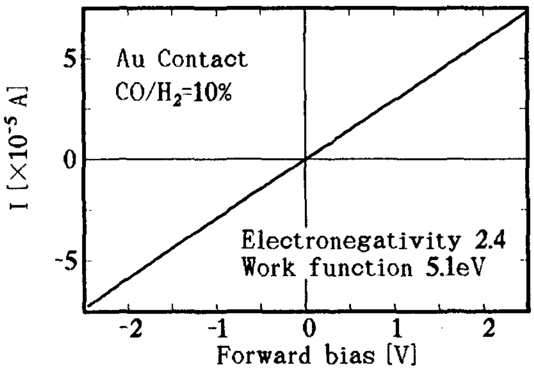

Fig. 3. I-V characteristics of an Au point contact to an as-deposited CVD diamond homoepitaxial film.

According to these results, CVD diamond has a remarkable property that I-V characteristics can be changed from rectifying to ohmic merely by changing the electronegativities of the metal. Also, the pinning of the Fermi level does not or less occur at the interface between the metal and diamond (001) surfaces.

In Si, large density of states (DOS) exists at the metal/semiconductor interface due to dangling bonds. If the dangling bonds at the surface of a semiconductor were terminated by hydrogen, the DOS at the semiconductor surface would be dramatically reduced. Although the reduction of the DOS at H-terminated Si surfaces has been reported by scanning tunneling spectroscopy (STS),[10] the metal contact properties associated with the low surface states density has hardly observed. The only one exception is reported on Hg/H-terminated Si.[11]

On the as-grown homoepitaxial CVD diamond (001) surfaces, the 2x1 reconstructed structure has been observed by RHEED and STM.[8] The surfaces are considered to be H-terminated due to their stability based on a calculation of energy[12] and their surroundings during deposition: H plasma. Furthermore, due to the stability of the C-H bonds, the H-terminated surfaces remain even after deposition of metal. In this respect, diamond is more suitable for the investigations of the metal/H-terminated interface than Si.

Our results show excessively strong dependence of the SBHs on the electronegativities of metals compared with that of other semiconductors which have less or no ionicity. Although diamond has no ionicity, the s factor of metal/diamond is about 0.7 in our rough estimation. This implies that nearly ideal Schottky contacts are obtained. Although it is unknown whether the unique characteristic of CVD diamond is caused by its H-terminated surfaces or its wide band gap, the former is more convincing due to the existence of the same phenomenon observed on Hg/H-terminated Si.[12] Other approaches of investigation, such as photoemission or thermal dependence of I-V properties, are required to obtain more information on the nature of H-terminated surfaces.

4. CONCLUSIONS

I-V characteristics were investigated using various metal contacts with CVD homo-epitaxial diamond films. Fourteen kinds of metals were used for point contacts and 5 kinds of metals for evaporated electrodes. The n factor of 1.01 was obtained when an Al point contact with CVD diamond was used. This value is the nearest to unity ever reported in diamond. The SBHs have a strong correlation with the electronegativities of metals. These are phenomena unique to as-deposited CVD diamond films. CVD diamond is one of the most appropriate semiconductors for investigation of metal/H-terminated semiconductor interfaces.

5. ACKNOWLEDGEMENTS

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