

Total Photoyields from CVD Diamond Surfaces and Their Electron Affinity

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Dependences of total photoyields on incident photon energies were measured using synchrotron radiation light for different chemical-vapor-deposited diamond with differently treated surfaces. Results show that a considerable amount of gap states are presented for as-grown specimens with H-terminated surfaces, that negative electron affinity (NEA) is realized for H-plasma-treated specimens, and that sufficient O-treatment to NEA specimens results in positive electron affinity. The observed electron affinity can be explained in terms of differences in strength of the surface dipole layer formed by difference in the electron negativity among C, H and O atoms.

Key words : Diamond, Electron affinity, Photoyields, Hydrogen detection

I. Introduction

One of the most attractive features of wide-gap diamond is its negative electron affinity (NEA), for which the minimum energy of the conduction band is located at a higher energy than the vacuum level, since the NEA property can lead to attractive application of diamond to bright electron emitter devices.¹⁾ In the case of natural diamond, in 1979 Himpfel *et al.* reported that diamond (111) surface has very high quantum yield (electrons per photon) which increases with incident photon energy and is more than 20% at 9 eV.²⁾

For practical applications, the property of diamond in films should be investigated. In 1994, we reported that the electron affinity is negative for both (111) and (100) surfaces of hydrogen-plasma-treated diamond crystal while both surfaces have a positive electron affinity study, we analyzed in more details, the photoyield data and the electron affinity of borondoped CVD diamond crystal with (111) and (100) surfaces covered with hydrogen and/or oxygen atoms.

II. Experimental

Diamond films were epitaxially grown on highpressure-synthesized crystalline diamond (111) and (100) surfaces by means of microwave plasma chemical-vapor-deposition (CVD) method. Boron doping was performed for all the specimens subjected to photoyield measurements in order to prevent the specimens from charging during the measurements. The details of diamond growth have been published elsewhere.^{3,4)} Hydrogen-adsorbed surfaces were obtained by exposing the specimens to hydrogen

plasma while oxygen-adsorbed ones were obtained by annealing in oxygen atmosphere. Total photoyield measurements were performed using ultraviolet lights either from the 750-MeV synchrotron orbital ring (SOR) at Oka-zaki, Japan or conventionally from a deuterium lamp. A quartz window was used to eliminate higher-order lights of energy > 8 eV. The amounts of H atoms on surfaces were determined on the basis of elastic recoil detection analysis (ERDA) data measured using a Pelletron accelerator⁴⁾ while Rutherford backscattering spectrometry (RBS) and Auger electron spectroscopy (AES) were employed to estimate the amounts of O atoms on specimen surfaces.

III. Result and Discussion

Figure 1 shows square root of total photoyield I versus incident photon energy for H-adsorbed (100) and (111) surfaces. In the low photon energy region below 6 eV, there were linear relations between $I^{1/2}$ and the energy. The thresholds of the photocurrent were located well below the diamond band gap energy of 5.5 eV. A theoretical study by Kane showed that $I^{1/2}$ should vary as a linear function of photon energy in the case of surface imperfection states distributed in energy in the case of surface imperfection states localized in energy.⁵⁾ This means that the H-adsorbed as-grown (100) and (111) surfaces of CVD diamond have a considerable amount of energy-distributed imperfection states in the band gap. We found, based upon transmission electron microscope (TEM)⁶⁾ and photoluminescence (PL)⁷⁾ measurements, that the as-grown CVD diamond has defective layer of nanometers in thickness. This imperfection is considered

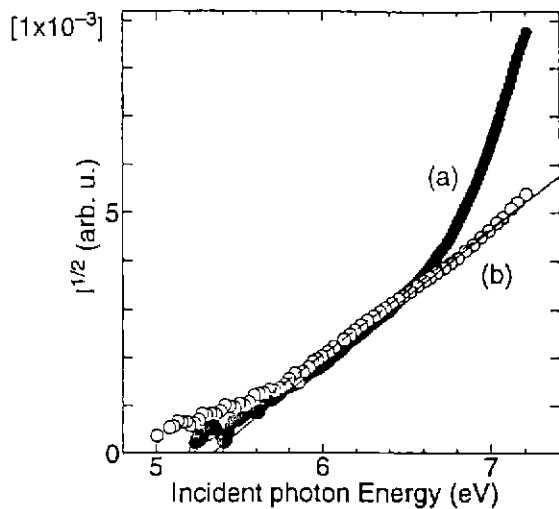


Fig. 1. Square root of total photoyield from hydrogen-adsorbed diamond as a function of incident photon energy: (a) (100) and (b) (111) surfaces.

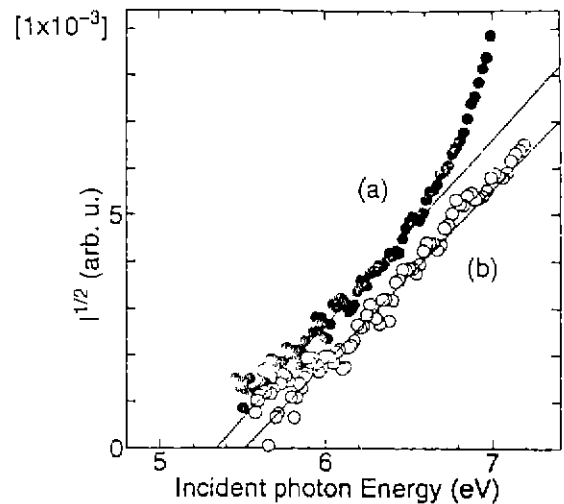


Fig. 3. Square root of total photoyield from diamond after irradiation of ultra-violet white lights as a function of incident photon energy: (a) (100) and (b) (111) surfaces.

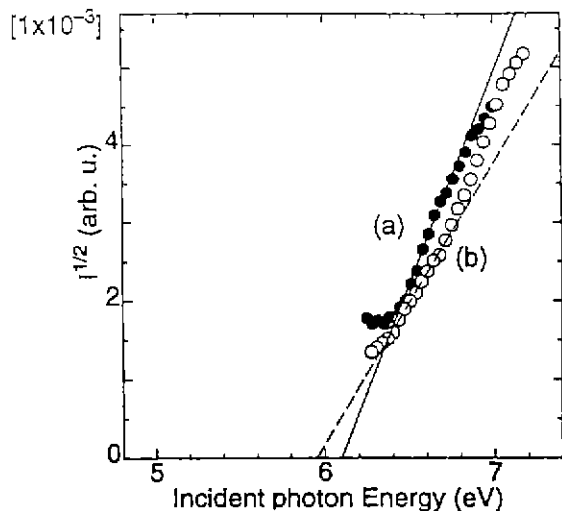


Fig. 2. Square root of total photoyield from oxygen-adsorbed diamond as a function of incident photon energy: (a) (100) and (b) (111) surfaces.

to be not due to the boron doping but to the plasma employed for the growth since similar surface defects can be observed for undoped specimens. In case of the presence of large amounts of gap states, it is not simple to determine whether the electron affinity of the specimen is non-positive or not.

On the other hand, as shown in Fig. 2, the threshold energies increased significantly for O-adsorbed (100) and (111) diamond surfaces, indicating a significant increase in the electron affinity and substantial elimination of the gap states observed for the asgrown specimens. This agrees well with TEM results showing a much thin surface imperfection layer.⁶ Because ERDA measurements show the presence of a considerable amount of H atoms for the O-adsorbed diamond,³ the bonding structure of the O atoms, which were detected by means of both RBS and AES tech-

niques,³ is not so simple that one should consider a complex of CO, CH and OH bonds on the specimen surface.

After white (zero-order) SOR lights were irradiated sufficiently to the O-adsorbed specimens in the vacuum chamber used for the photoyield measurements, $I^{1/2}$ was again well fitted in the low energy region by a linear or slightly superlinear function of the incident photon energy for both (100) and (111) surfaces. The threshold energies obtained for both surfaces were located near the band gap energy. The above theory tells that $I^{1/2}$ varies linearly with photon energy for the volume processes in the case of indirect optical excitation although a similar relation between the total photoyields and incident photon energy can be applied to a case of "rough" surface working as momentum absorber.⁵ The above TEM results for the O-adsorbed specimens strongly suggest that the former process (bulk effect) should be more important for the O-adsorbed specimens. It should be mentioned that in this case the band bending effect is not important for the doping density obtained.

Since the electron affinity is determined by both the surface effect related to the surface potential structure and the bulk effect related to the multi-body effect among valence electrons of C atoms, the above results indicate the importance of the surface effect. The surface imperfection layer of nanometers in thickness for the as-grown CVD diamond can be substantially removed by means of the O treatment. The large shifts of the threshold energy come from the change in the surface dipole potential energy between the different adsorbates on the diamond surface. The differences in the electronegativity among C, H and O atoms can be responsible for the differences in the dipole energy. In other words, attraction of electrons by the adsorbed O atoms from the surface C atoms causes a dipole to the surface C atoms lead to a dipole layer with a positive surface.

However, the surface atomic structure of the specimens were not analyzed in the present study, further investigations are required to completely understand the photoemission property in the case of the presence of adsorbates on the CVD diamond surface. Since the total photoyield is determined by both the photon adsorption process and the electron diffusion process to the specimen surface, the crystalline quality is important especially near the threshold photon energy due to main electron-hole pair creations in a deep diamond region of sub-micron meters.

IV. Conclusions

We have measured total photoyields from H-and/or O-adsorbed (100) and (111) surfaces of CVD diamond. On one hand, in both (100) and (111) cases, as-grown H-terminated surfaces have negative electron affinity with surface defective layer which yields photoemission at photon energies below the diamond band gap of 5.5 eV. On the other hand, O-adsorbed surfaces are characteristic of positive electron affinity. After the elimination of the O

atoms by sufficient irradiation of white lights in the ultra-violet region to the specimens in vacuum, both the (100) and (111) diamond surfaces have non-positive electron affinity with much smaller amounts of gap states, compared with the as-grown CVD diamond.

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