

Structure and reactivity of single crystal diamond surface

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1. Introduction

The diamond films have been studied extensively in recent decade, due to the attractive character of diamond, i.e., the highest hardness among all the materials, wide band gap, widespread transparency range from ultraviolet to infrared radiation, etc. Diamond was generally deposited on substrate by chemical vapor deposition method (CVD) from a hydrocarbon as a carbon source diluted with an amount of hydrogen. To date, however, we have faced several problems to utilize diamond films for practical applications, for example as hard coating, optical coating and electric devices. The first approach to solve these problems could be to clarify the mechanism of diamond growth in thermodynamically metastable conditions. Generally, to investigate the mechanism of CVD process, we must study three kinds of steps in CVD process; a) gas phase reaction, b) transport phenomena from gas phase to substrate, c) surface reaction. Many researchers tried to study two of them, gas phase reaction and transport phenomena, on diamond CVD process. On the other hand, few researches on the characteristic of diamond surface were reported by surface scientists who might be less interested in diamond CVD process.

From less knowledge of diamond surface, the electric conductivity of diamond surface was well known to be dependent on the species, which terminated the dangling bonds on diamond crystal surface. That is, H-terminated surface is p-type conductive, while O-terminated surface is insulating. Moreover, H-terminated surface might have negative electron affinity, while O-terminated has positive. It was confirmed that diamond film surface deposited by CVD methods is terminated with H atoms, due to the mixture of hydrogen and hydrocarbon as source gas. Compared with Si, H-terminated surface of diamond is extremely stable in air for a long duration. Therefore, this p-type surface would be promising to develop the novel type of electric device. Since surface H atoms have the intensive effects on electronic properties, it is important to detect H densities either on surface or in the vicinity of surface. Unfortunately, however, these densities were still unknown due to no precise measurement techniques.

Therefore, we are now investigating the kinetic interaction of H and O atoms included in source gas on diamond surface, using the surface science technique. The other target is to develop the quantitative detection method of atomic H on diamond surface using a resonance nuclear reaction, and to clarify the relationship between H atomic density and surface electronic properties.

2. Radical reaction on diamond surface

The (111) natural diamond crystal ($\phi 8$) was located in UHV chamber with LEED, TDS, AES and XPS. The (111) surface was reconstructed into 2×1 structure after annealing of over 1450K. Even 0.05ML dosing of H atoms enabled the surface structure to be recovered into 1×1 . The H-terminated 1×1 surface was exceptionally stable up to 1400K. AES fine spectra could detect both the H absorption and the surface structure, which were identical with the results of LEED and TDS. The peak temperature of H thermal

desorption was around 1300K.

Now, using IIb type diamond synthesized under thermodynamically stable condition (high pressure condition), we are trying to investigate the interactions of H and O atoms on (001) surface. We will be able to report the results of these interactions in the near future.

3. Quantitative measurement of H atom density

The H atom measurements both of polycrystalline film on Si and of (001) epitaxial film on Ir were performed in an UHV chamber using 2C beam line at the Research Center for Nuclear Science and Technology at the University of Tokyo. $^{15}\text{N}^{2+}$ beam was accelerated to energy of 6.3–6.6MeV and injected normal to the sample. The resonance nuclear reaction $^1\text{H} (^{15}\text{N}, \alpha \gamma) ^{12}\text{C}$ has occurred when ion with 6.385MeV meets ^1H atom. Meanwhile, H atom present in the film can react with ion accelerated over resonance energy, which penetrates into the film and loses the kinetic energy down to the resonance energy, by the collisions with carbon atoms. Detection of γ rays emitted as a result of the nuclear reaction enables us to measure the H concentrations.

Figure 1 shows the γ -ray intensity profile as a function of the ion energy taken from as-deposited diamond film. The profile reveals a peak around the resonance energy. Comparing with the reference, the surface density is around $8.8 \times 10^{14} \text{ cm}^{-2}$ for polycrystalline film. This density was about half the dangling bond density on ideal (111) surface. H concentration in the films was almost independent on the depth from the surface. The H bulk concentration was estimated to be $3.9 \times 10^{20} \text{ cm}^{-3}$, which corresponded to H/C ratio 0.22at%. On the other hand, the dangling bonds on (001) epitaxial film were almost fully terminated with H atoms. The H bulk concentration was estimated to be $1.4 \times 10^{20} \text{ cm}^{-3}$, which corresponded to H/C ratio 0.08at%. This is due to the fact that epitaxial film had less grain boundary region.

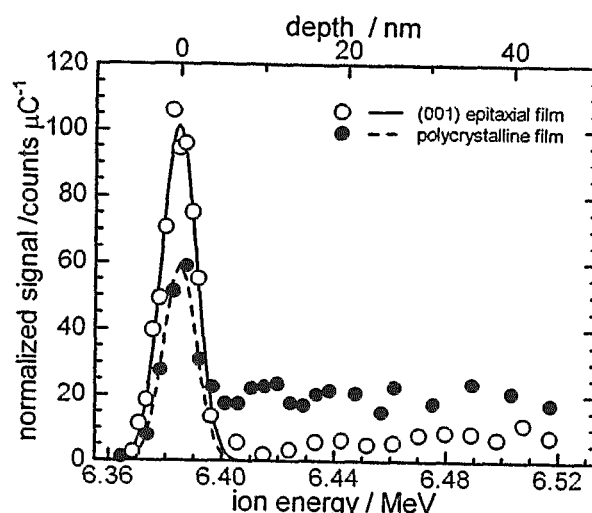


Fig. 1 Intensity profiles of the γ ray emitted from the resonance nuclear reaction of $^1\text{H} (^{15}\text{N}, \alpha \gamma) ^{12}\text{C}$, as a function of the incident $^{15}\text{N}^{2+}$ energy taken for the as-deposited diamond film.