

## Initial Stages of Cu Surfactant Growth on Sb-Adsorbed Diamond Surfaces

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Initial stages of Cu overgrowth on diamond films using surfactant atoms such as arsenic and antimony have been investigated by synchrotron radiation photoelectron spectroscopy. While arsenic does not adsorb on diamond surfaces, antimony adsorbs in the physisorption mode, which is converted to the chemisorption mode by annealing. The effect of Sb surfactant atoms on Cu overlayer morphology and Cu-diamond interfacial properties is also revealed.

### 1. Introduction

The surface electronic properties of diamond are of interest in understanding groupIV semiconductor surfaces. Diamond-based semiconductor devices are applicable for high temperature operation and metal/insulator/metal (MIM) resonant tunneling operation. These applications will require hetero-epitaxial crystal growth of metal and semiconductor films.

Since Cu ( $a=3.61496\text{\AA}$ ) is closely lattice matched to diamond ( $a=3.56683\text{\AA}$ ), Cu is expected to form an epitaxial overlayer. However, almost no work has been reported on the interfacial chemistry or electronic properties of this system. In this study, we investigated initial stages of Cu overgrowth on diamond films using surfactant atoms such as arsenic and antimony in comparison to the hydrogen-terminated diamond surfaces that are formed by etching diamond in HF solution.

### 2. Experimental

Experiments were performed at beamline 1A of the Photon Factory in KEK. For surface sensitive information, synchrotron radiation photoelectron spectroscopy (SRPES) with photon energy of about 100 eV was performed, and for C 1s core levels, X-ray photoelectron spectroscopy (XPS) was used. Poly-crystalline diamond films<sup>1)</sup> with a grain size of about 1 to 3  $\mu\text{m}$  were grown on Si(111) p<sup>+</sup> wafers by plasma chemical vapour deposition (CVD) with CO + H<sub>2</sub> gas at 40 Torr for 4 hours. The HF-etched diamond surface showed a RHEED (reflection high

energy electron diffraction) ring pattern. After the specimen was annealed at about 600 °C in an MBE chamber, the ring pattern was almost unchanged. An As or Sb flux beam from conventional K-cells was irradiated onto the clean surface at various temperatures in the MBE chamber.

Then, Cu was deposited on the adsorbed diamond surfaces at room temperature. Cu was also deposited on H-terminated diamond surfaces<sup>2)</sup> cleaned with a 20-25 % HF solution. Surface morphology was investigated by AFM (Atomic Force Microscopy).

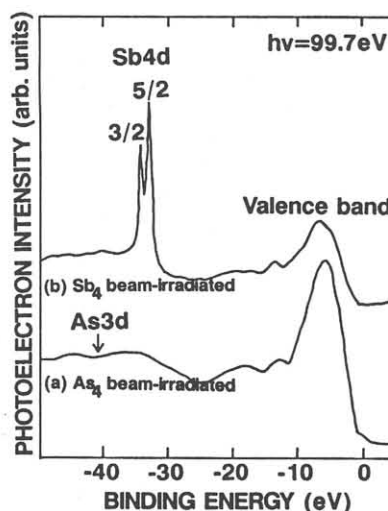


Fig. 1 Photoelectron spectra from diamond surfaces irradiated by As and Sb beams.

### 3. Results and discussion

#### 3.1 As and Sb adsorption on diamond films

We tried to terminate the diamond surface with As and Sb, both well-known surfactant materials<sup>3)</sup>. Figure 1 shows photoelectron spectra taken from the diamond surfaces on which an As<sub>4</sub> beam or a Sb<sub>4</sub> beam was irradiated at room temperature (RT). Although the As<sub>4</sub> beam was also irradiated onto the surface at 200 °C, 400 °C, and 500 °C for 30 sec, no As adsorption was observed. Since Williams et al.<sup>4)</sup> reported that InAs can be grown on diamond(001) between 250 °C and 470°C, the In top layer was thought to play a key role in InAs growth. When we deposited less than one monolayer of In on diamond, we found that As atoms adsorbed on the In surface of about 70%, judging from the As3d and In4d photoelectron intensities. Therefore, it can be concluded that the formation of In-C bonds on the diamond is important in the InAs growth process.

On the other hand, strong Sb4d 5/2 and 3/2 peaks were clearly observed on diamond. Figure 2 shows Sb4d photoelectron spectra taken from the Sb<sub>4</sub> beam-irradiated diamond surfaces at RT and 200 °C. The chemical shift of Sb4d toward lower binding energy by 0.5 eV caused by 200°C annealing can be attributed to the change in bonding from physisorption to chemisorption, that is the formation of Sb-C bondings. The drastic difference between As and Sb adsorption features may be explained by the existence of Sb<sub>2</sub> molecules in the Sb flux from the conventional K-cell. Moreover we may also have to consider the higher vapour pressure of As than Sb. The adsorbed Sb on diamond desorbed with vacuum annealing at 300°C.

#### 3.2 Cu overlayer growth on H/diamond and Sb/diamond

Next, we deposited Cu metal on both H-

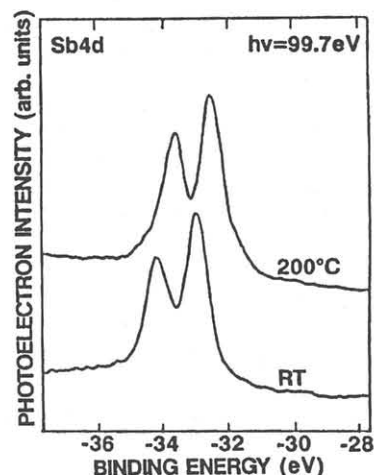
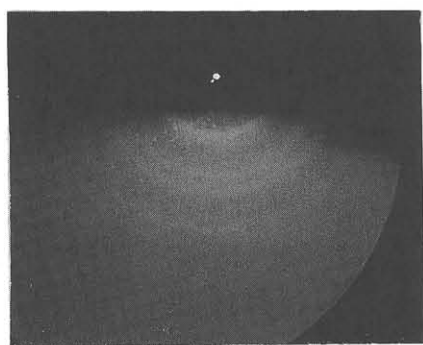


Fig. 2 Sb4d photoelectron spectra from the Sb-deposited diamond surface at room temperature and the 200 °C-annealed surface.

terminated and Sb-adsorbed diamond surfaces at RT. Figure 3 shows RHEED ring patterns for Cu films with and without the Sb overlayer. At the initial stage of Cu deposition a significant difference was observed in the inner ring pattern. While Cu on the H-terminated surface showed almost the same ring pattern as the H/diamond having a single inner ring pattern, the Sb-adsorbed surface showed a double ring pattern. When more than 20 Å of Cu was deposited, the inner ring became a clear double ring pattern for both surfaces. Therefore the Sb layer is thought to enhance surface migration of Cu on diamond at the initial stage of growth to easily form Cu clusters at kink sites. This is the first Sb surfactant effect.

The Cu surface morphology was analyzed by AFM. Figure 4 exhibits AFM images of Cu-deposited surfaces on polycrystalline diamond grains about 2 μm in size. The Cu overlayer on Sb/diamond is rougher than that



(a) Cu/diamond(111) (b) Cu/Sb/diamond(111)

Fig. 3 RHEED patterns for Cu thin films (about 10 Å) on diamond (111) surfaces (a) without and (b) with the Sb overlayer. The electron energy for RHEED was 20 keV.

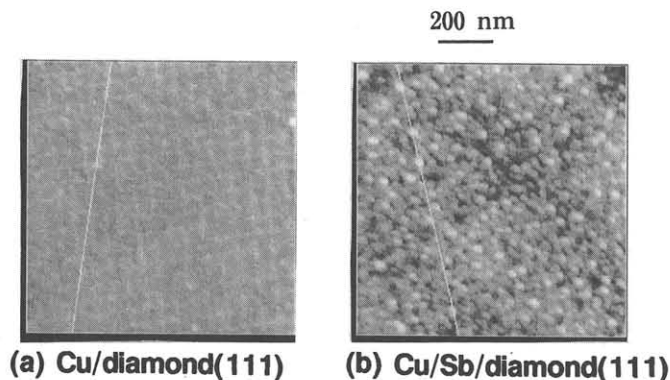


Fig. 4 AFM images of Cu-deposited surfaces on (a) H-terminated diamond and (b) Sb-adsorbed diamond. The images are  $1\mu\text{m}$  wide.

on H/diamond. The AFM line analysis revealed that Cu/Sb/diamond has many cones about 4-6 nm high and about 20-30 nm wide, while the Cu/H/diamond surface is about 1-2 nm high. This is the second Sb surfactant effect which is well correlated to the first effect.

The Cu growth mechanism was investigated by SRPES and XPS. The Sb4d peak intensity remains almost unchanged upon Cu deposition on the Sb-adsorbed diamond surface up to  $10\text{\AA}$ , which is probably because the Cu overlayer grows in a strong island growth mode. However, the Sb4d peak drastically decreases for more Cu deposition, suggesting that almost all the Sb-adsorbed layer remains at the Cu-diamond interface having stable Sb-C bonds. This phenomenon seems to be different from the ordinary surfactant epitaxy, where the surfactant atoms segregate to the overlayer surface, resulting in the layer-by-layer mode growth<sup>3)</sup>. However, we have found another unique surfactant phenomenon similar to this Cu/Sb/diamond in the case of  $\text{SrF}_2/\text{As}/\text{InP}$ , where the As layer of about 2 ML on InP remains at the interface strongly changing the morphology of the epitaxial  $\text{SrF}_2$  films<sup>5)</sup>. The Cu3d peak positions for the Cu/Sb/diamond had a binding energy (B.E.) of 4.1 eV at the first Cu deposition (about  $10\text{\AA}$ ) and 3.1 eV at deposition of about  $700\text{\AA}$ , while those for Cu/H/diamond had B.E. of 3.7 eV at the first Cu deposition and 3.1 eV at  $700\text{\AA}$ . Thus, Cu3d peak energies appear at higher binding energy for the Cu/Sb/diamond. This is the third Sb surfactant effect.

In order to investigate the effect of the Sb layer on metal-diamond contact formation, XPS C1s spectra were analyzed. When Cu was deposited on clean diamond surface, the C1s peak drastically shifted toward higher binding energy by about 0.46 eV, as shown in Fig. 5 (a), suggesting downward band bending, that is a higher hole Schottky barrier height. In contrast, a small C1s peak shift was observed for the

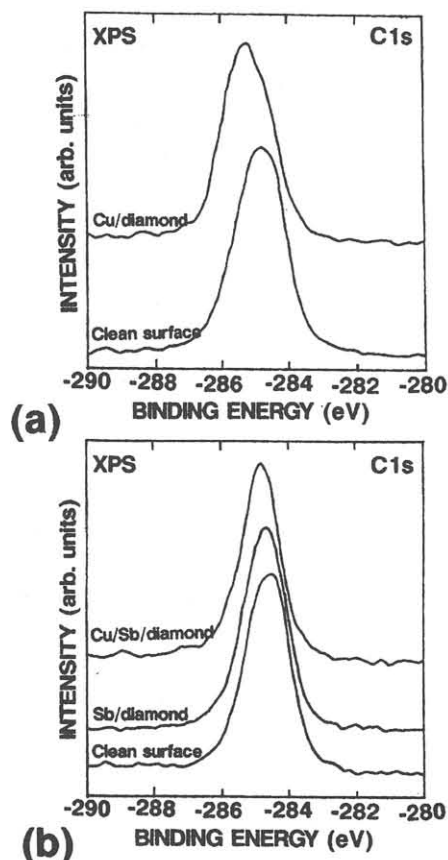


Fig. 5 XPS C1s spectra for (a) Cu/diamond surfaces and for (b) Cu/Sb/diamond surfaces.

Cu/Sb/diamond case, as shown in Fig. 5 (b). This result indicates that the Sb atoms act as a buffer layer to prevent the Cu-diamond interfacial reaction which disrupts the diamond surface.

These four Sb surfactant effects may be correlated, resulting in higher surface migration of Cu with less Cu-diamond reaction, and the formation of a lower Schottky barrier height and clustered Cu surface.

#### 4. Conclusion

While arsenic does not adsorb on diamond surfaces, antimony adsorbs in the physisorption mode, which is converted to the chemisorption mode by annealing. Cu deposition on H- and Sb-terminated diamond surfaces shows four Sb surfactant effects with respect to surface morphology and electronic properties, which can be explained by the stable Sb-C bonds enhancing surface migration of Cu atoms.

#### References

- 1) H. Kawanada et al., Proc. ISCSI-1, 1994 Elsevier Science B.V., p.161.
- 2) W.R.L. Lambrecht, Physica B 185 (1993) 512.
- 3) M. Copel et al., Phys. Rev. Lett. 63(1989)632.
- 4) K.E. Williams et al., Appl. Phys. Lett. 61(1992) 405.
- 5) S. Heun et al., 3rd Int'l Symp. on Atomic Layer Epitaxy, 1994, Sendai, pp. 52.