Advanced Materials '93, I / B: Magnetic, Fullerene, Dielectric, Ferroelectric,
Diamond and Related Materials, edited by M. Homma et al.
Trans. Mat. Res. Soc. Jpn., Volume 14B

Atomic scale observations of CVD diamond surfaces by STM

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The scanning tunneling microscopy (STM) has been employed to the observations of CVD homoepitaxial diamond (001) and (111) surfaces. The dimer type 2x1 reconstructed structure has been observed on (001) surfaces. Isolated dimer rows and antiphase boundaries where out of phase dimer rows meet have been observed. These features suggest the dimers play an important role for growth of CVD diamond. On (111) surface, monohydride 1x1 structure with 0.25nm spacing was observed. Some adsorbates different from the monohydride structure have been found on each terrace.

1. INTRODUCTION

In recent years, many studies of the diamond synthesis by chemical vapor deposition (CVD) method have been reported. However, the studies of CVD diamond surfaces have just started. The studies of the surface structure are very important to solve growth mechanisms and surface electronic properties for instance. Since the surface energy of diamond is extremely high, low order index surfaces, i.e. (001) or (111) surfaces, tend to appear on diamond poly-crystalline films after growth. In other words, it is suggested that these surfaces become smooth in atomic level. That's to say, these low order index surfaces are proper to apply to the studies of surfaces.

The 2x1 reconstruction has been confirmed on CVD homoepitaxial diamond (001) surface by RHEED[1]. The atomic scale observations of the surface by STM have been reported for the first time in 1991 by Tsuno et al.[2]. But discussions of detailed configurations of the surfaces have been just started.

There are some reports of the diamond (111) surface. Yamada et al. reported that the clean (111) surface forms 2x1 structure and 1x1 structure appears when the surface is exposed to more than 0.05 monolayer of hydrogen atoms. The STM observations have been carried out in only a few reports[3,4].

In this report, we have performed the atomic scale observations of these low order index surfaces by STM, and discussed the more detailed atomic configurations of these surfaces.

2. EXPERIMENTAL PROCEDURES

Diamond homoepitaxial films were grown by means of a conventional microwave plasma-assisted CVD method on high-pressure synthetic type Ib diamond (001) and (111) substrates. The source gas was CO (5vol%) diluted with hydrogen. The total gas flow rate was 200 SCCM, and the total pressure was 35 Torr. The substrate temperatures during the deposition were 850°C on (001) surface, and 940°C on (111) surface. The deposition time was normally 3 hours (thickness of the film was about 1μm).

STM observations were carried out under atmospheric pressure after deposition.

3. RESULTS AND DISCUSSION

Figure 1 is a typical STM image of the undoped homoepitaxial diamond (001) surface. Dimer rows elongated to the two equal <110> directions are seen, i.e. (001) surface reconstructs to the double domain 2x1/1x2 structure. Dimer rows were observed reproducibly over all scanned areas. Average terrace size of this sample is about 10nm. The distance between two dimer rows was measured 0.5 nm corresponding to two lattice constants of (001) surface. In this image, a dimer row extending to the direction of the row (marked "a") is seen, and two dimer rows including a few dimers (marked "b") exist stably. These rows ("a" and "b") suggest that the growth of diamond occurs in the direction of these rows. We varied the applied tip bias voltage in the range from 0.1V to -0.1V during the observations, but the images were not dependent on the bias voltage.

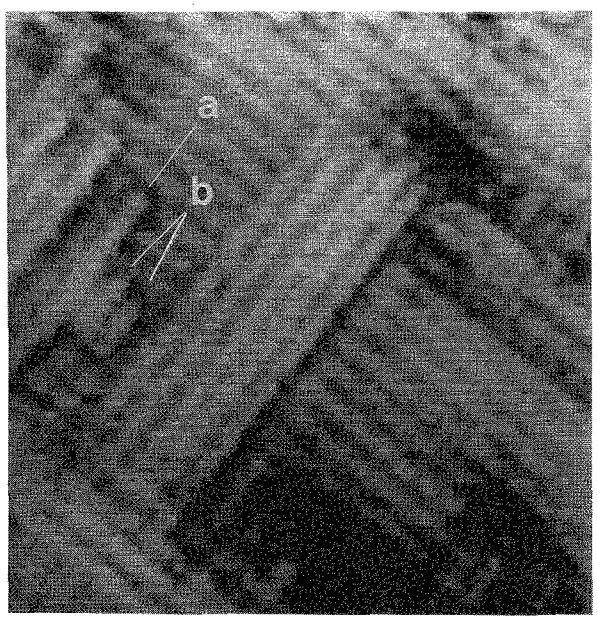


Fig. 1. A typical STM image of undoped diamond (001) surface. Tip bias and tunneling current were 0.1V and 3nA.

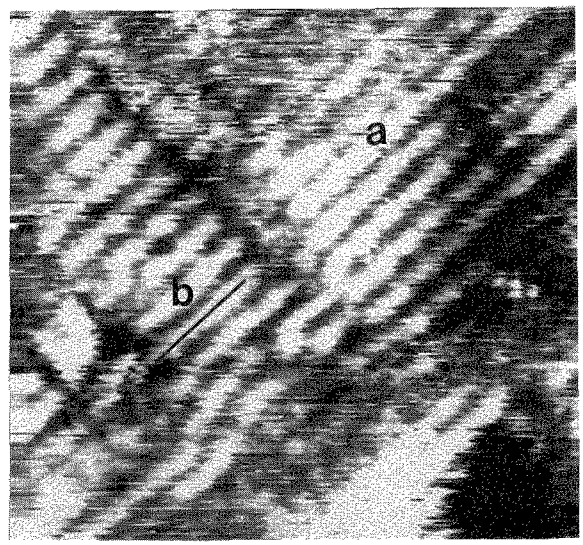
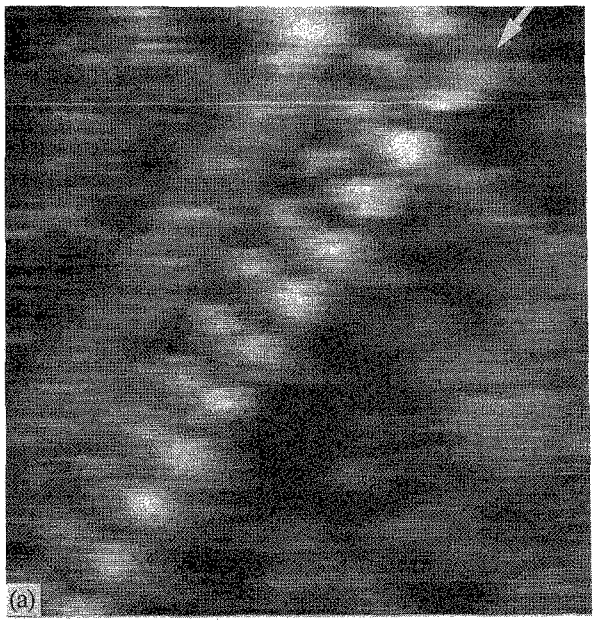
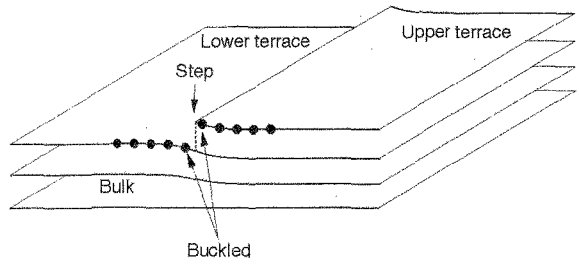


Fig. 2. An antiphase boundary of the diamond (001) surface. Tip bias and tunneling current were -0.05V and 1nA.

Figure 2 is an image of a discontinuous boundary. The line drawn in this figure passes through the dimer rows in region "b", but coincides with the trough between the dimer rows in region "a". This boundary is called an 'antiphase boundary'[5]. The antiphase boundary may be formed where the dimer rows of each domain meet out of phase during growth, and suggests that the epitaxial growth of diamond is achieved through the extension of dimer rows.

Figure 3(a) is a high-resolution image of the step edge. The upper terrace is on the left-hand side and the lower is on the right-hand side of this image. The dimer atoms at the step edge (marked by an arrow) are observed to be 0.05nm higher than the adjacent dimer atoms in the same dimer row[5]. In typical STM images (Fig. 1), symmetric dimers were usually observed, but Fig. 3(a) appeared to be asymmetric. In the case of Si (001) surfaces, asymmetric dimers on a lower terrace at the step edge have been observed[6]. In this reference, the lower dimer atoms at the step





(b)

Fig. 3. (a). A high resolution image of a step. Dimer atoms next to the step edge (marked by an arrow) are uplifted. Tip bias and tunneling current were 0.05V and 3nA. (b). A schematic illustration of a step including a general understanding of relaxation (cross sectional view).

edge were observed to be lower than the adjacent dimer atoms in the same dimer row. Our image of asymmetric dimers is consistent with the images in this reference, and with the general understanding of atomic step structure shown in Fig. 3(b).

We also performed the observations of (111) homoepitaxial films. Figure 4 is a typical STM image of the surface. In this image, atom-like dots are clearly observed, and the distance between two nearest dots is 0.25nm. It corresponds to the distance between two carbon atoms of diamond (111) ideal surface. Since atomic hydrogen is dense in the deposition atmosphere, each dangling bond of diamond (111) 1x1 may be terminated by one hydrogen atom. This monohydride model is shown in figure 5[7].

In figure 4, some adsorbates are observed besides the atom-like dots. Well resolved image of this adsorbates is shown in figure 6. A special feature of the adsorbates is its ring-like shape. This ring-shaped images are very similar to the SiH_3 images on HF-treated Si (111) surfaces[8]. On the other hand, there

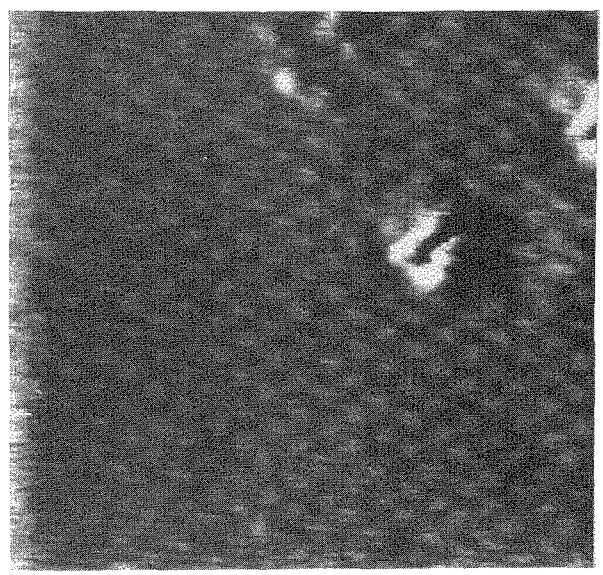


Fig. 4. A typical STM image of undoped diamond (111) surface. Tip bias and tunneling current were 0.05V and 1nA.

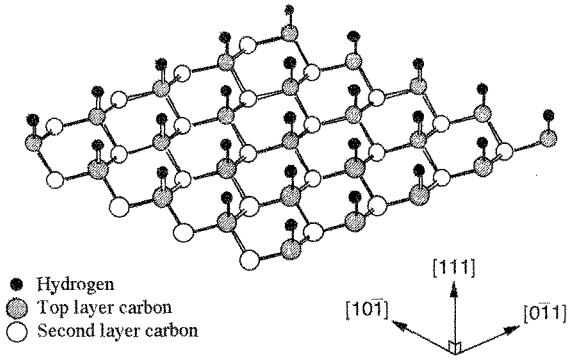


Fig. 5. Structure model of diamond (111) 1x1-H. Each dangling bond is terminated by one hydrogen atom (monohydride model).

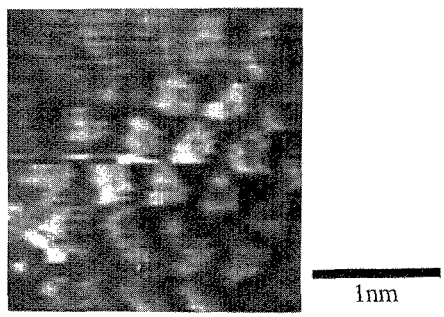


Fig. 6. An ring-shaped adsorbates image. These adsorbates are on $\sqrt{3}x\sqrt{3}$-R30° positions.

are some reports suggesting that CH_3 radicals can adsorb on the diamond (111) surfaces. From these circumstance, we speculate the ring-shaped adsorbates are trihydride CH_3[7]. Further experiments are needed to determine this structure precisely.

4. CONCLUSIONS

Atomic scale observations of homoepitaxial CVD diamond (001) and (111) surfaces have been performed by STM in atmospheric pressure. On (001) surface, 2x1/1x2 reconstructed structure has been observed reproducibly. The following local arrangement have been found in detailed observations: 1)antiphase boundary, 2) asymmetric dimers at step edge. On (111) surface, monohydride 1x1 structure has been confirmed. However, ring shape adsorbates have been observed, and we speculate these adsorbates are trihydride CH_3.

ACKNOWLEDGEMENTS

The authors would like to thank Mr. R. Hasunuma, and Prof. I. Ohdomari for their collaboration and advice, Mr. S. Yamashita of Tokyo Gas Co. Ltd., and Mr. N. Fujimori of Sumitomo Electric Industries Ltd., and Mr. K. Nishimura of Osaka Diamond for their cooperation. This work was supported in part by Grant-in-Aid for General Scientific Research (Grant NO. 04650658) from the Ministry of Education, and Culture of Japan.

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