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STM Observation of Diamond(111) Epitaxial Films

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Epitaxial films were grown on diamond(111) substrates by microwave-plasma-assisted chemical vapor deposition, and their surfaces were studied by scanning tunneling microscopy. The images were obtained with atomic order resolution. The surface showed a 1x1 structure and the steps were very straight, indicating an addition of growth units at kinks.

1. INTRODUCTION

The mechanism of chemical vapor deposition (CVD) of diamond[1] has not been understood clearly, although more than a decade has past since Matsumoto et al. established diamond CVD[2]. To elucidate the mechanism, both vapor phase reactions and surface reactions should be studied. Observation of the growth surface is important for the elucidation of the growth mechanism, as the growth process affects the structure of the growth surface such as surface reconstruction, steps and islands. Scanning tunneling microscope (STM) can provide this information with very high resolution, and it is an invaluable method for the study of diamond CVD growth.[3-5] In this report, the observation of epitaxial films on (111) single-crystalline substrates is presented.

2. EXPERIMENT

Epitaxial growth were performed on type Ib synthetic single-crystalline diamonds. The (111) substrates were cleaved, cut, mechanically polished and cleaned using chromic acid. Before deposition, the substrates were cleaned in acetone by ultrasonic cleaning, and also in a mixture of HF and HNO_3 (1:1), then in a mixture of HCl and HNO_3 (1:3) and finally in de-ionized water. Epitaxial growth was carried out by microwave-plasma-assisted CVD[6] from a methane-hydrogen gas mixture. A $[CH_4]/[H_2]$ ratio of gas mixtures was in the range of 0.5 % to 6.0 %. The pressure and total gas flow were 60 torr and 200 sccm (standard cm^3 per minute), respectively. Measured by an optical pyrometer, the substrate temperature during growth was maintained at 850 °C. The diamond surface showed ample low electric resistance for STM observation as was reported by Nakahata et al.[7]

After the growth, the samples were removed into the normal atmosphere, STM images were observed in the normal atmosphere. The film thickness was measured by scanning electron microscopy observation of the cleaved faces and was found to be in the range of 0.5 μm to 1.0 μm.

3. RESULTS AND DISCUSSION

Figure 1 shows the LEED pattern of an as-grown surface with $[CH_4]/[H_2]$ =

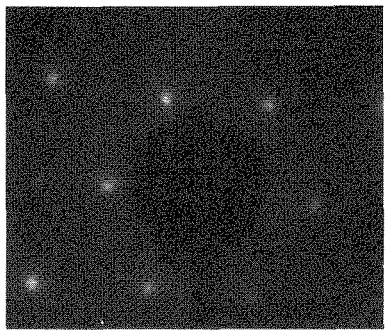

FIG. 1 LEED pattern of diamond(111) after epitaxial growth.

1%, indicating a 1x1 surface. Figs. 2(a) and (b) show the STM images with a 100 nm square area for the surfaces grown with different $[CH_4]/[H_2]$. At a lower methane concentration, the surfaces show a triangular structure[8]. As the methane concentration became higher, these triangular features were distinguished and islands showed a round shape.

Explicit observation was carried out on the flat areas of the triangular structure. Figs. 3(a) and (b) are the STM images of (111) terrace with atomic order resolution, showing 1x1 periodicity. At the lower left corner in Fig. 3(b), a step can be seen, which corresponds to single bi-atomic height.

Many steps were seen even on the flat areas on the islands. Most of them are toward the <112> direction, resulting in the triangular structure. The majority are single bi-atomic steps. Double bi-atomic steps were also often observed with a wide step-to-step distance. Besides <112> steps, $<11\bar{2}>$ steps were also observed. STM images of these three types were shown in Figs. 4(a)-(c). The result that the step height corresponds to single or double bi-atomic heights, suggests the growth of single bi-layer unit. The steps in

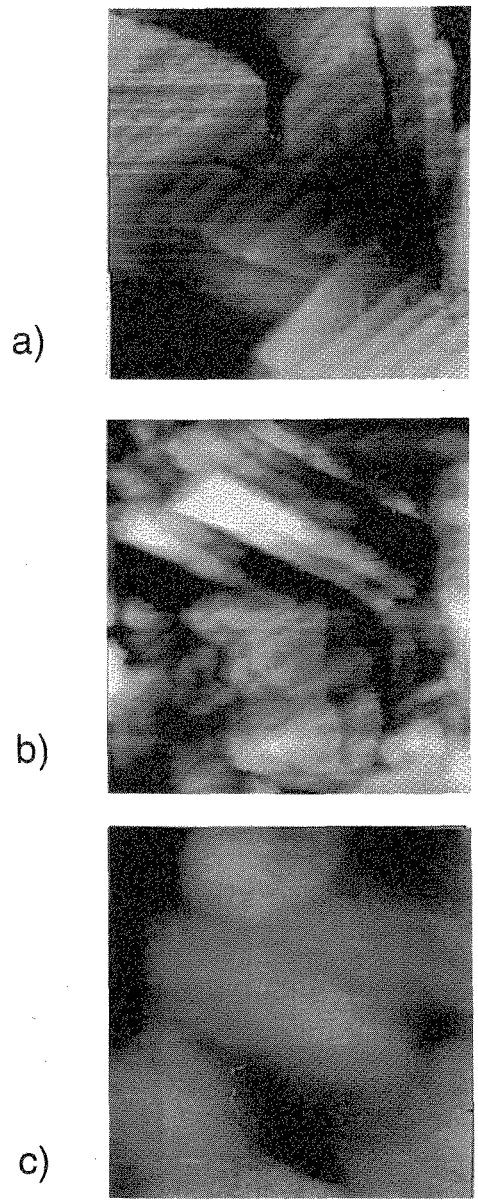

FIG. 2 STM images of diamond(111) epitaxial surfaces in 100nm square. $[CH_4]/[H_2]$ during growth was a) 1% b) 2% and c) 3.5%. Tip bias and tunneling current are 0.5 V and 2.0 nA, respectively.

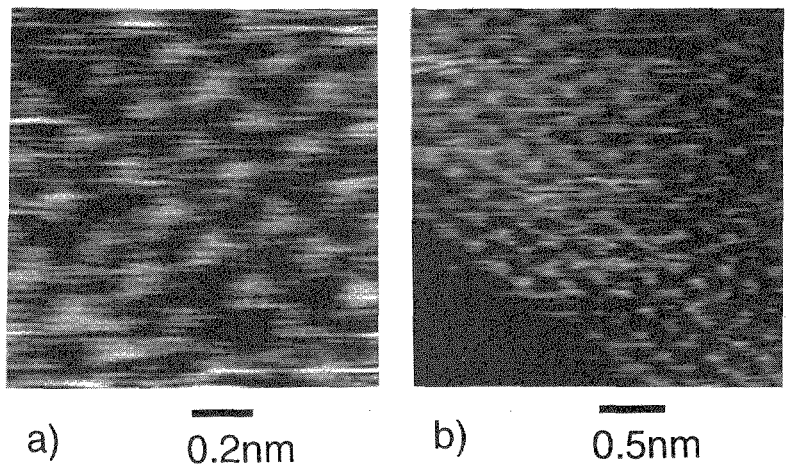

FIG. 3 STM images of diamond(111) epitaxial films. Sample bias and tunneling current are 0.1V and 2nA for (a), 0.2V and 0.5nA for (b).

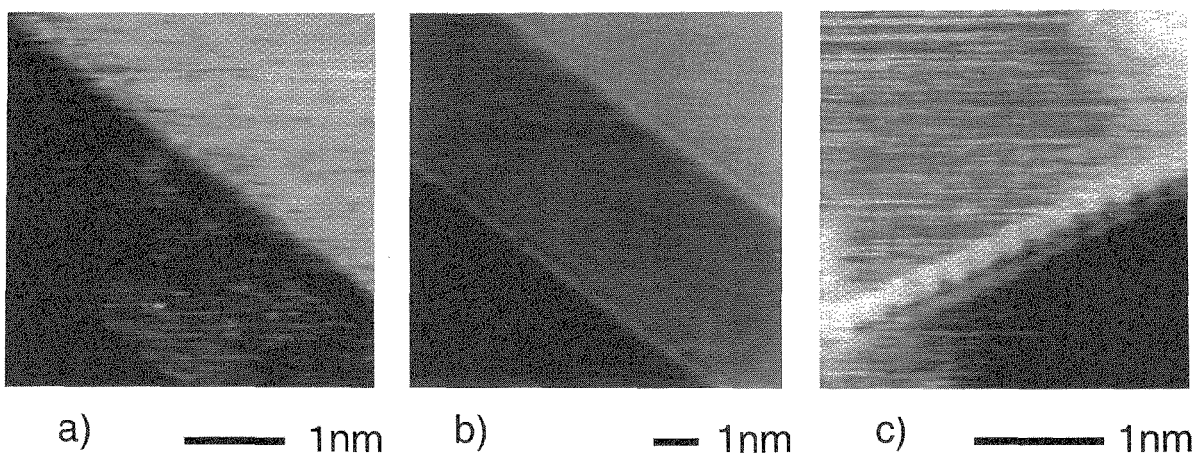

FIG. 4 STM images of steps on diamond(111) epitaxial films. (a) <112> single bi-atomic steps, (b) <112> double bi-atomic steps and (c) <11$\bar{2}$> single bi-atomic steps.

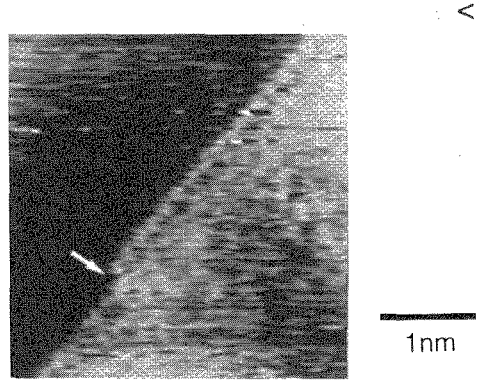

FIG. 5 Constant current mode STM image of <112> single bi-atomic layer step. Sample bias and tunneling current are 0.5 V and 1.0 nA, respectively. A kink is pointed by an arrow.

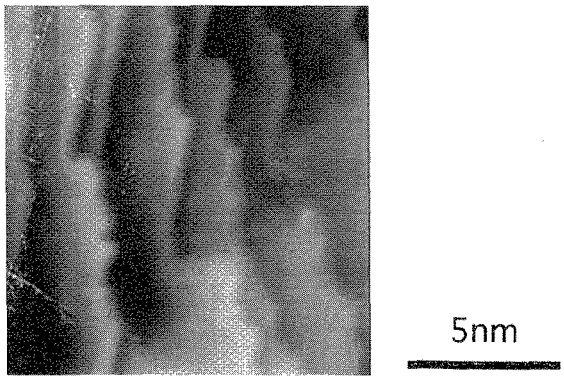

FIG. 6 Constant current mode STM image of diamond(111) epitaxial film grown with [CH4]/[H2]=3.5%.

Figs. 4 show a very straight shape, which suggests the instability of kink and the main incorporation of carbon atoms at the kink. The kinks of the surface 1x1 unit were observed at intervals in the main type <112> single bi-atomic step. The typical image of the kink is indicated by the arrow in Fig. 5.

At a higher methane concentration, the islands do not have a triangular structure but a round shape as is seen in Fig. 2(c). The magnified image shown in Fig. 6 exhibits bi-atomic height steps again, suggesting the bi-layer growth.

4. CONCLUSION

STM observation with atomic order resolution was performed on diamond (111) epitaxial surface. The terrace showed flat 1x1 images and steps showed single or double bi-atomic height. This suggests that the surface structure is uniform over the entire (111) terraces and that the growth unit in (111) epitaxial growth is bi-atomic. The steps showed a straight edge shape in the atomic scale and kinks of the surface 1x1 unit was observed at intervals. This suggested that the dominant incorporation of carbon atoms is performed at the kinks.

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