Interface study of heteroepitaxial diamond films on silicon (001) substrates

Ke-an Feng, Jie Yang, and Zhangda Lin
The State Key Laboratory of Surface Physics, Institute of Physics, Chinese Academy of Science, Beijing 100080, People's Republic of China
(Received 17 June 1994; revised manuscript received 12 September 1994)

Locally epitaxial diamond films on mirror-polished Si(001) substrates have been prepared by using surface-biasing pretreatment in a hot-filament chemical-vapor-deposition system in our laboratory. The diamond is in epitaxial alignment with the silicon substrate, with approximately diamond (001) parallel to Si(001) and the [110] directions of the epitaxial layer parallel to the silicon surface. High-resolution cross-sectional electron microscopy clearly shows that there are about 40 rows of carbon-atom planes on 25 rows of silicon-atom planes in the observed epitaxial interface. The dislocation density is very high in the interface, but the diamond $(\bar{1}1\bar{1})$ planes are shown to be continuous across the interface with 7.3° towards [001]. The three components of dislocations that are formed at the interface are discussed. The interfacial tilting and azimuthal rotational misorientation are shown to come from these dislocations. The relationship between the tilting angles and high-misfit-dislocation density is analyzed.

I. INTRODUCTION

The heteroepitaxy of diamond films via chemical vapor deposition is required for the practical use of diamond of various forms in various applications.[1,2] Single-crystal thin films of diamond have great potential for high-temperature electronic devices, if the films can be grown heteroepitaxially on an Si substrate. But the growth of diamond deposited on all nondiamond substrates is impeded by the difficulty of nucleation, due to lattice mismatch or lack of chemical bonding at the interface,[3] so it is necessary to explore the heteroepitaxial technological conditions and to understand the physical and chemical processes of the heteroepitaxial interface.

Recently Yoshikawa *et al.*[4] reported that cubic boron nitride (*c*-BN), which has almost the same lattice parameter as that of diamond, could be used as a substrate for the epitaxial growth of diamond. Unfortunately, *c*-BN substrates of sufficient size that make the diamond growth process practical are unavailable at the present time. The epitaxial diamond film growth on single-crystal SiC via bias-enhanced microwave plasma chemical vapor deposition was performed by Stoner and co-workers.[5,6] Zhu *et al.*[7] presented the micrograph of the scanning electron microscopy of the diamond grown at the center or the edge regions of a β-SiC(001) substrate. The epitaxial relationship between the diamond and SiC was confirmed by cross-sectional transmission electron microscopy (TEM) and transmission electron diffraction (TED). The epitaxial growth of local diamond films on (100)Si substrates has been reported.[8,9] Recently, Jiang and co-workers[10,11] reported successful synthesis of continuous diamond films grown heteroepitaxially on a mirror-polished single crystalline silicon (001) substrate by microwave plasma chemical vapor deposition from a methane/hydrogen gas mixture, and the morphology of the deposited diamond film was characterized by using scanning electron microscopy, Raman spectroscopy, and x-ray analysis. Their results demonstrated that the diamond crystallines are oriented to the silicon substrate with both the (001) planes and the [110] direction parallel to the silicon substrate, although the big lattice mismatch (diamond/Si) existed in the local epitaxial interface. But information of the detailed heteroepitaxial film for the diamond (001)/Si(001) interface has not been presented previously.

We have presented[12] the local epitaxial diamond film on a mirror-polished Si(001) substrate with surface biasing pretreatment prepared by hot-filament chemical-vapor-deposition (HFCVD) mix gas flow H_2/CH_4, in terms of the lattice image of high-resolution cross-sectional electron microscopy (HREM) and the interface pattern of the selected area TED. Results about the interface arrays were obtained: the diamond film was oriented to the silicon substrate with approximately both (001) planes and [110] directions parallel to the silicon substrate, very high misfit dislocation density existed at the interface; it is shown as a 7.3° angle on the diamond (001)/Si(001) interface. Here, we will explain the relationship between the tilting angle 7.3° on diamond (001)/Si(001) and a very high misfit dislocation density on the heteroepitaxial interface (001).

II. EXPERIMENTS

For the heteroepitaxial film between diamond and silicon, due to the big mismatch of 35% between diamond ($a=3.57$ Å) and silicon ($a=5.44$ Å), the epitaxial film is formed directly from the Si substrate without any intermediate layer in the real interface, although the dislocations and deformation of the diamond atoms array relative to Si atoms in the interface exist. The epitaxial array in Fig. 1 show clearly that at least 40 rows of diamond atoms on diamond (001) planes are consistent with 25 rows of silicon atoms on Si(001).

The misorientation and epitaxial relationship are described in Fig. 2. In this [110] projection, the diamond $(\bar{1}1\bar{1})$ planes are shown to be continuous across the inter-

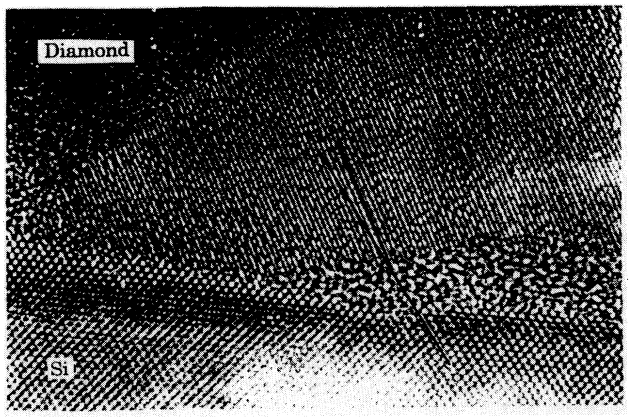

FIG. 1. Micrograph of HRETM about the epitaxial diamond/Si interface. The specimen was observed in the [110] direction.

face (001), but the 7.3° tilting of the diamond $(\bar{1}1\bar{1})$ planes towards the [001] direction was noted.

The pattern of TED in Fig. 3 display that the diamond $(\bar{1}1\bar{1})$ spots are rotated with the angle 10.7° about the Si[110] axis relative to the silicon $(\bar{1}1\bar{1})$ spots.

Kobayashi, Kardsawd, and Watanabe reported[13] that TEM studies of the diamond/Si interface have found a 2-nm-thick amorphous layer between the Si and the polycrystalline diamond, which was also observed in some parts of the interface in our sample.

The local epitaxial layer in Fig. 1 clearly shows that diamond epitaxy on Si occurs not only on an intermediate silicon carbide layer but also directly on the Si substrate under suitable conditions.

III. THEORETICAL ANALYSIS

The structures of the amorphous and twin regions in Fig. 1 are complicated. Here we focused only on the morphological analysis of the local epitaxial layer.

If the mismatch on the heteroepitaxial growth film is within about 20%, the Hooke law on elastic mechanics

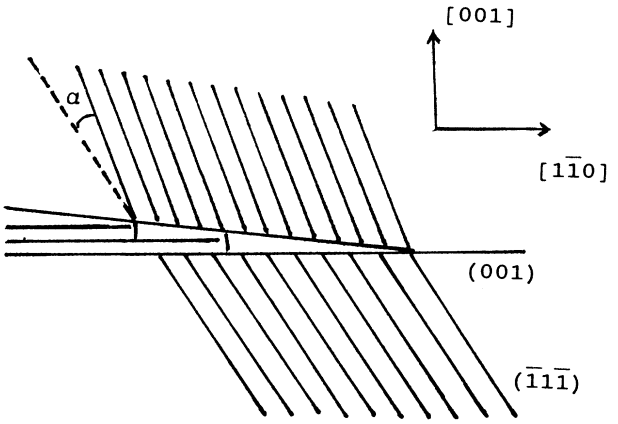

FIG. 2. Diagram of a relationship between misorientation and tilting angle at the interface (001).

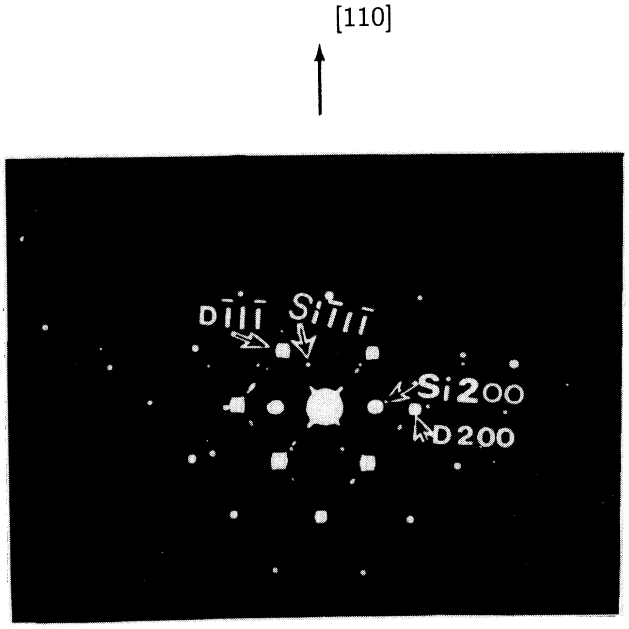

FIG. 3. Selected-area pattern of TED on the diamond/Si interface. Here, *D* indicates diamond.

can be applied: the strains of the adsorption atom array are proportional to the tensile stress in the film plane. A common conclusion[14] for elastic deformation of heteroepitaxial interface is that the misfit dislocation density is about 14%, which is equivalent to the dislocation spacing measured as, on average, one misfit dislocation every seven lattice planes. In the case of the lattice parameter mismatch of 18% for the diamond (a=3.57 Å)/β-SiC (a=4.36 Å) interface, the elastic deformation mechanism is valid, so that the misfit dislocation density of 14% is shown in the HRTEM of a diamond/β-SiC interface.[6,7] Stoner *et al.* have explained the 5° tilting angle of the diamond $(1\bar{1}1)$ planes towards the $[\bar{1}10]$ direction when the diamond $(1\bar{1}1)$ planes are continuous across the interface in terms of 14% dislocation density and 60° mixed type dislocation interface.[6,15]

The local array (40 rows/25 rows) on a small diamond/Si epitaxial interface in Fig. 1 demonstrated that one misfit dislocation relates to an average of 2.67 lattice planes, corresponding to the dislocation density 0.375 in the interface regions. Obviously, the misfit dislocation density is larger than 14%.

From Fig. 1 and Fig. 3, we confirmed that the diamond $(\bar{1}1\bar{1})$ plane not only rotated about the Si[110] axis, but also the plane has the misfit along $[\bar{1}10]$. From the lattice structure of the Si(001) substrate and the experimental micrograph, we suggest that three components of dislocations may form at the interface: one component [001] of the Burgers vector perpendicular to the boundary plane (001) to accommodate tilt (forming the familiar tilt boundary) and a second component $[\bar{1}10]$ of the Burgers vector lying in the interface to accommodate interfacial misfit, the third component [110]-azimuthal rotation. Both the tilt ($\mathbf{b}_1$) and misfit ($\mathbf{b}_2$) components are pure-edge type dislocations, while the azimuthal rotation com-

ponent $\mathbf{b}_3$ involves a pure screw-type dislocation, so that the Burgers vector of the dislocation at the diamond/Si heteroepitaxial interface will have a vector $\mathbf{b}=\sqrt{11}\,a/4\,[\bar{1}31]$; the tilting component $\mathbf{b}_1$ in the [001] direction will have an angle 72.45° with $\mathbf{b}$ in Fig. 4.

The magnitude of the tilting angle resulting from an array of pure horizontal dislocations may be written from the relationship[16]

$$\sin\alpha=\frac{|\mathbf{b}_1|}{D},$$

where D is the dislocation spacing with $|\mathbf{b}_1|=0.302\times|\mathbf{b}|$. We also have that $D=d/\rho$ (2), where ρ represents the misfit dislocation density per$\{111\}$ lattice plane along the $[\bar{1}10]$ direction and d is the spacing between (111) planes. With b and d expressed as a function of the lattice parameter a, $|\mathbf{b}|=\sqrt{11}a/4$, $d=2a/3$, Eq. (1) may be used to calculate the interfacial tilting angle α to be approximately 8.08°, which is in good agreement with that measured from HREM in Fig. 1. Therefore, it can be concluded that the very high dislocation density is most likely responsible for the observed interfacial tilt. Using a similar approach and the twist boundary model, the angle of azimuthal rotation involving the screw component $|\mathbf{b}_3|=0.420|\mathbf{b}|$ can be obtained as $\beta=11.27°$, which is also in good agreement with the measurements in the diffraction pattern of TED in Fig. 3.

It is interesting to point out that in the elastic deformation scope, a common conclusion—misfit dislocation density 0.14—is consistent with the measurements on the heteroepitaxial interface between diamond and β-SiC, which have about 20% lattice mismatch. But in the deformation of the adsorption atom array with the big lattice mismatch, the Hooke law for elastic deformation cannot be used; the misfit dislocation density in the interface will be increased as the lattice mismatch increases. The crystallographic information for diamond (001)/Si(001) heteroepitaxial interface showed the nonelastic deformation and the big misfit dislocation density.

In terms of the Auger electron and thermal-desorption spectroscopies, Jackman, Chud, and Foord discussed[17] recently the initial stages of diamond film growth with hot-filament-activated methane and hydrogen on Si(001). Under the initial growth conditions, the clear and ordered Si(001)-2×1 substrate is determined by low-energy electron diffraction and Auger electron spectropy methods. Owing to the atomic array and lattice strains on the [110] direction inconsistent with that on $[\bar{1}10]$ for the Si(001)-2×1 surface, so that two dislocation components $\mathbf{b}_2$ and $\mathbf{b}_3$ are not the symmetric parts of the Burgers vector $\mathbf{b}$, means that the dislocation which is showed on the diamond (001)/Si(001) interface does not belong to the 60° mixed-type dislocation.

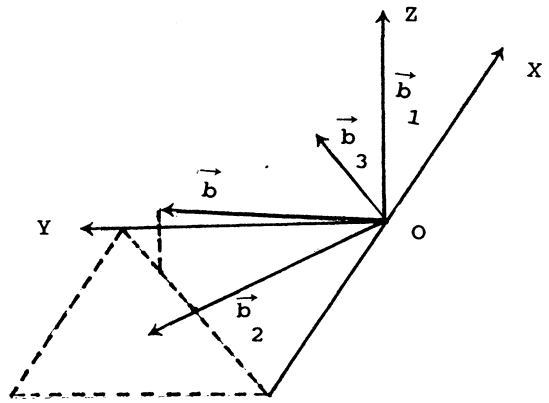

FIG. 4. The decomposition of dislocation at the diamond/Si interface into tilt ($\mathbf{b}_1$), misfit ($\mathbf{b}_2$), and azimuthal rotation ($\mathbf{b}_3$) components.

Both materials (silicon and carbon) are covalently bonded crystals. Thus the heteroepitaxial films can be grown successfully when the correct choice of the nucleation condition is applied, even if a large mismatch between covalent bond crystals of the adsorption and substrate exists. The local epitaxial diamond film on Si(001) (in Fig. 1) is a good example. The attempts to understand the microscopic reactions and the initial growth which form the diamond film on Si(001) are in progress.

IV. CONCLUSION

The local heteroepitaxial diamond film crystals on a mirror-polished silicon wafer have been prepared by an improved HFCVD method involving pretreatment and growth. In this paper, the micrograph of high-resolution cross-sectional TEM at the heteroepitaxial interface diamond (001)/Si(001) has been analyzed. The misfit dislocations observed in diamond film not only accommodate the misfit strain but also cause both interfacial tilting and azimuthal rotational misorientation. Our studies have made clear the reason for the experimental results of the heteroepitaxial diamond film on Si(001).

ACKNOWLEDGMENTS

The authors wish to acknowledge financial support from the Nature Science Foundation of China (NSFC) and AST 863 program.

[1]W. A. Yarbrough and R. Messier, Science **39**, 1 (1989).
[2]W. A. Yarbrough, J. Vac. Sci. Technol. A **9**, 1145 (1991).
[3]T. Suzuki, M. Yagi, and K. Shibuki, Appl. Phys. Lett. **64**, 557 (1994).
[4]M. Yoshikawa, H. Ishida, A. Ishitani, T. Murakami, S. Koizumi, and T. Inuzuka, Appl. Phys. Lett. **57**, 428 (1990).
[5]B. R. Stoner and J. T. Glass, Appl. Phys. Lett. **60**, 698 (1992).
[6]B. R. Stoner, G. H. M. Ma, S. D. Wolter, W. Zhu, Y-C. Wang, R. F. Davis, and J. T. Glass, Diamond. Relat. Mater. **2**, 142 (1993).
[7]W. Zhu, X. H. Wang, B. R. Stoner, G. H. M. Ma, H. S. Kong, W. H. Braun, and J. T. Glass, Phys. Rev. B **47**, 6529 (1993).
[8]J. Narayan, A. R. Srivatsa, M. Peters, S. Yokota, and K. V. Ravi, Appl. Phys. Lett. **53**, 1823 (1988).

[9]D. G. Jeng, H. S. Tuan, R. F. Salat, and G. J. Fricano, Appl. Phys. Lett. **56**, 1968 (1990).
[10]X. Jiang and C. P. Klages, Diamond. Relat. Mater. **2**, 1112 (1993).
[11]X. Jiang, C. P. Klages, R. Zachai, M. Hartweg, and H. J. Fussner, Appl. Phys. Lett. **62**, 3458 (1993).
[12]Jie Yang, Zhangda Lin, Li-Xin Wang, Sung Jin, and Zhe Zhang, Appl. Phys. Lett. (to be published).
[13]K. Kobayashi, S. Karasawa, and T. Watanabe, J. Cryst. Growth **99**, 1211 (1990).
[14]J. H. van der Merwe, J. Appl. Phys. **41**, 4725 (1970).
[15]H. Olsen and M. Ettenberg, in *Crystal Growth, Theory and Techniques,* edited by C. H. L. Goodman (Plennum, New York, 1978), Vol. 2.
[16]D. A. Porter and K. E. Easterling, *Phase Transformations in Metal and Alloys* (Van Nostrand Reinhold, New York, 1981), p. 117.
[17]R. B. Jackman, L. H. Chua, and J. S. Foord, Surf. Sci. **292**, 47 (1993).

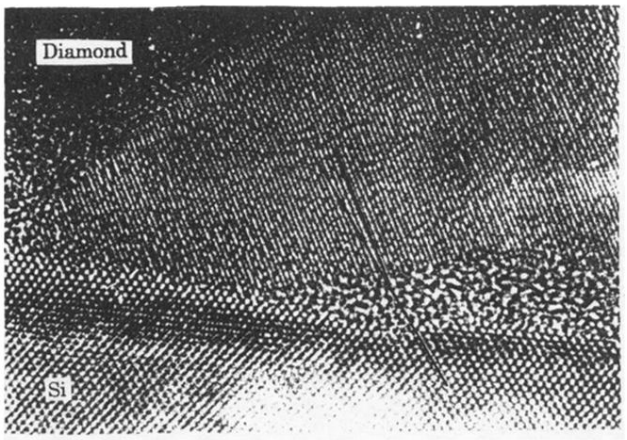

FIG. 1. Micrograph of HRETM about the epitaxial diamond/Si interface. The specimen was observed in the [110] direction.

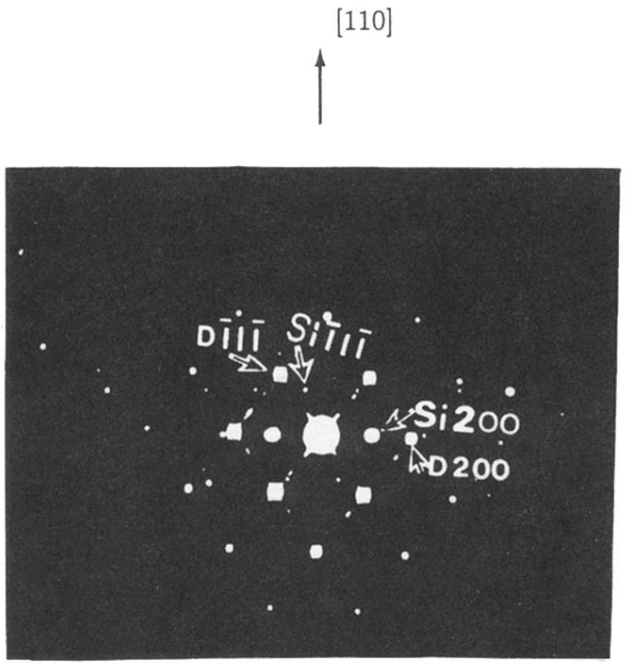

FIG. 3. Selected-area pattern of TED on the diamond/Si interface. Here, *D* indicates diamond.