Role of hydrogen in the initial stage of diamond heteroepitaxy on silicon

S.-T. Lee and Y. W. Lam
Department of Physics and Materials Science, City University of Hong Kong, Kowloon, Hong Kong

Zhangda Lin, Yan Chen, and Zhiqing Gao
State Key Laboratory of Surface Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100080, China

(Received 26 March 1996)

The reaction of atomic hydrogen with the C_2H_2-covered Si surface was studied using high-resolution electron-energy-loss spectroscopy (HREELS), thermal-desorption mass spectrometry (TDMS), and low-energy electron diffraction. We found that atomic hydrogen broke up the carbon-carbon bond in C_2H_2 and the Si-Si dimers on the Si surface, which led to the formation of C-H and Si-H bonds, respectively. When the C_2H_2-covered Si(100) surface was exposed to a filament-activated H_2/CH_4 mixture, HREELS showed that the C-H stretching signal grew at the expense of the Si-H stretching signal. This observation was consistent with the replacement of the Si-H bond by $-CH_3$, possibly following hydrogen abstraction from the Si-H bond by atomic hydrogen. TDMS analysis showed significant desorption of atomic hydrogen at both 650 and 750 K and a little desorption of CH_2 and CH_3 only at 650 K, although HREELS remained unchanged with annealing temperature. This showed that part of the hydrocarbon species on the Si surface existed as a stable network of hydrocarbon, which possibly was the initial stage of diamond formation on Si. [S0163-1829(96)00540-1]

I. INTRODUCTION

It is well known that diamond is an outstanding material for high-temperature electronic devices, but the rarity and high cost of diamond crystals have severely hampered the development of diamond electronics. To obtain a large diamond monocrystal, diamond heteroepitaxy on a suitable substrate is an attractive approach. Jiang and Klages[1] of the Fraunhofer Institute in Hamburg and Wolter *et al.*[2] of North Carolina State University have made a great stride towards diamond heteroepitaxy on Si. Both groups achieved the growth of highly oriented polycrystalline diamond on Si. More recently, Lin and co-workers also reported the local epitaxy of diamond (100) (Ref. 3) and (111) (Ref. 4) on Si(100). More importantly, Jiang and Klages and Lin *et al.* showed that in the interface region diamond grew directly on Si with no interlayer such as SiC. This observation provided further insight into diamond heteroepitaxy on Si; although the epitaxial area is only about 5×5 μm^2.

In order to understand the mechanism of local epitaxy of diamond on Si and consequently to possibly achieve the large area growth of monocrystalline diamond, it is important to understand the initial stage of diamond epitaxy on Si. Quite recently, Ogitsu *et al.*,[5] through *ab initio* calculations of carbon atoms on a diamond (001)-(2×1):H surface and of silicon atoms on Si(001)-(2×1):H surface, found that hydrogen atoms migrated spontaneously on a diamond (001) surface and acted as a surfactant during diamond (001) homoepitaxy. This theoretical work represents just a beginning effort in this fruitful field; clearly continual and more in-depth study is warranted.

For the diamond growth via low-pressure chemical vapor deposition (CVD), the gaseous sources of CH_4, C_2H_2 and H_2 are involved and the role of atomic hydrogen is widely recognized. To simulate this growth process, we conducted a systematic study of the interaction between activated H_2/CH_4 and C_2H_2 absorbed on Si (100)-(2×1) surface. Our objective is to gain more insight into the mechanism of diamond heteroepitaxy and the important role of atomic hydrogen in CVD diamond growth on Si. Some of the results can further act as useful guides towards achieving heteroepitaxial growth of diamond on Si.

II. EXPERIMENT

Experiments were conducted in an ultrahigh vacuum chamber which housed a Leybold ELS-22 high-resolution electron-energy-loss spectrometer (HREELS), four-grid retarding field analyzer for normal-incidence low-energy electron diffraction (LEED) and Auger electron spectroscopy (AES), and a quadruple mass spectrometer (QMS). The base pressure obtained in the chamber was about 5×10^{-11} mbar.

Atomic hydrogen dosing was accomplished by exposing the sample to hydrogen heated by a tungsten filament coil ($\phi3$ mm$\times$30 turns with $\phi0.3$ wire). The gaseous sources (high-purity hydrogen and acetylene) were leaked into the chamber separately through a stainless steel doser which was positioned close to the filament.

N-type (Sb-doped) 0.7-Ωcm Si (100) wafer with a size of $16\times8\times0.5$ mm^3 was used as a substrate. The Si sample was grasped tightly by a Ta piece at both ends and heating was effected by passing a dc through the Si piece. After careful cleaning, the Si wafer was installed into the chamber. Under the pressure of 1×10^{-10} mbar, the Si wafer was heated at 1150 K for several hours, then flashed quickly to 1500 K for several cycles, and finally cooled down to 300 K. No oxygen and carbon contamination could be detected by HREELS and AES after the heat treatment, and the LEED pattern showed a (2×1) reconstruction. The adsorption of the acetylene onto the Si(100)-(2×1) surface was conducted under acetylene pressure of 5×10^{-8} mbar for different dosing time. The hydrogen leaked into the chamber only after

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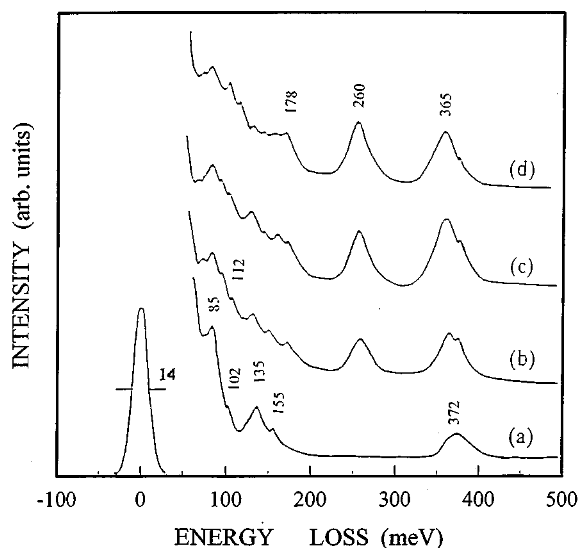

FIG. 1. HREELS of the interaction of atomic hydrogen with Si(100)-(2×1) surface preexposed to 4 L of C_2H_2. The amount of atomic hydrogen is measured in terms of the dose of filament-activated hydrogen; (a) 0 L, (b) 30 L, (c) 130 L, and (d) 430 L.

the residual acetylene gas had been pumped out (chamber attained 3×10^{-10} mbar). The filament that hanged at 4 cm from the substrate was heated to 2200 K, while the substrate temperature was kept lower than 350 K during hydrogen dosing.

The sample position was carefully reproduced for every HREELS measurement after each exposure. The primary energy of the electron beam was 4 eV and an incidence angle of 60° with respect to the surface normal was used. The off-specular angle $\Delta\theta$ is zero.

III. RESULTS AND DISCUSSION

With the base pressure at 1×10^{-10} mbar, C_2H_2 was leaked into the chamber to a pressure of 5×10^{-8} mbar and the Si(100)-(2×1) surface was exposed to C_2H_2 for 80 sec. Afterwards, C_2H_2 gas was pumped out and a vacuum of 3×10^{-10} mbar achieved within minutes. This exposure, equivalent to 4 L [1 L (Langmuir)$=1\times10^{-6}$ mbar sec], was chosen to ensure saturation coverage, as Nishijima *et al.*[6] and Yoshinobu *et al.*[7] reported that 2 L already resulted in saturation coverage. Our experiment also revealed that exposure as much as 400 L beyond 4 L did not induce any detectable change in HREELS.

Figure 1(a) shows the HREELS spectrum of a Si(100)-(2×1) surface after 4-L acetylene exposure. Intense losses were observed at 85, 135, and 372 meV and small losses at 102 and 155 meV. Meanwhile, the LEED pattern showed that there was no detectable change in the (2×1) reconstruction of Si(100) surface other than an increase of the background intensity. The present results are consistent with those of Nishijima *et al.*[6] and Yoshinobu *et al.*[7] showing that C_2H_2 adsorbed on a clean Si(100)-(2×1) surface was in the molecular form. The adsorbed C_2H_2 did not change the dimer structure of Si(100)-(2×1) and Si surface reconstruction remained. However, the carbon atoms in C_2H_2 were di-σ bonded to the adjacent Si atoms of a dimer on Si(100) as depicted in Fig. 2. According to the theoretical calculation of Craig and Smith[8,9] the C=C double bond just lay on the bridge of the Si-Si dimer. Referring to work by Nishijima *et al.*,[6] Yoshinobu *et al.*,[7] and a handbook,[10] the 372-meV loss peak in HREELS corresponds to the stretching vibration of C-H and the 155-meV-loss peak to the bending vibration of C-H in C_2H_2 adsorbed on Si. The loss peaks at 85 and 102 meV correspond, respectively, to the symmetric and asymmetric stretching vibration of SiC, while that at 135 meV is attributed to the C=C stretching vibration.

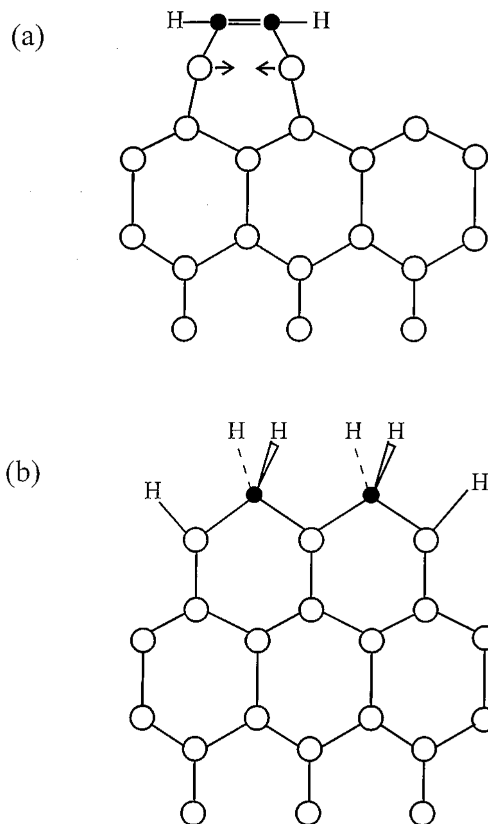

FIG. 2. Schematic illustration of C_2H_2 adsorption on Si(100)-(2×1) surface before (a) and after (b) interaction with atomic hydrogen. Open circles and black circles represents Si and C atoms, respectively.

When the C_2H_2/Si sample shown in Fig. 1(a) was exposed to H_2, neither the LEED pattern nor HREELS showed any change, indicating that molecular hydrogen did not interact with the surface to induce any changes. When the tungsten filament was heated to 2200 K and H_2 leaked into the chamber to 5×10^{-7} mbar for 1 min (equivalent to 30 L), the HREELS [Fig. 1(b)] showed a remarkable change. This shows that under the interaction of atomic hydrogen surface adsorption changes dramatically. In addition to the peaks shown in Fig. 1(a), new peaks appeared at 365, 260, 178, and 112 meV. The 365-meV loss peak corresponds to the C-H stretching vibration of singly or sp^3 bonded carbon, 260 meV to the Si-H stretching vibration, 178 meV to the C-H scissor vibration, and 112 meV to the C-H rocking vibration. Meanwhile, the LEED pattern, although remained mainly as the (2×1) reconstruction, yet the intensities of the $\frac{1}{2}$ points became weaker. This is interpreted to mean that the (1×1)

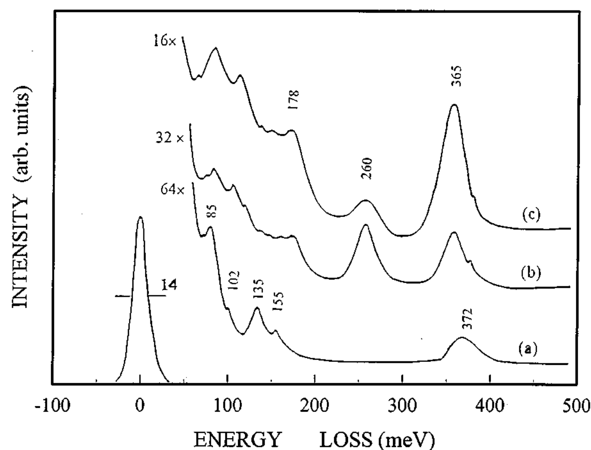

FIG. 3. HREELS of (a) 4-L C_2H_2 preadsorbed Si(100)-(2×1) surface [same as Fig. 1(a)], (b) after 430-L exposure to atomic hydrogen [same as Fig. 1(d)], and (c) after an additional 300-L exposure of a filament-activated mixture of H_2 and CH_4.

domain has appeared. From these results, we deduce that, by the action of atomic hydrogen, the double bond of the C=C dimer [see Fig. 2(a)] on the Si surface was broken and was replaced by two C—H bonds resulting in the formation of $C<^{H}_{H}$, which gives rise to the C-H stretching vibration at 365 meV, scissor vibration at 178 meV, and rocking at 112 meV, respectively. Concomitantly, the Si-Si dimer was opened by the action of atomic hydrogen to form a Si-H bond which accounts for the prominent loss peak at 260 meV. Due to the breaking of the C=C double bond and the Si-Si dimer, the released atoms returned to their respective stable position equivalent to that of bulk atoms, so the (1×1) LEED pattern appeared. Figure 2 illustrates schematically the Si and C atom positions before and after interaction with atomic hydrogen.

At 4-L C_2H_2 and subsequent exposure to atomic hydrogen with 30-L H_2, the C=C and Si-Si dimers on Si surface were only partially released; thus both C and Si exist in two bonding configurations on the Si(100) surface, resulting in the coexistence of the (2×1) and (1×1) surface structures. As a result, the LEED pattern and HREELS spectra demonstrated an overlap of these two phases. With the dosing of atomic hydrogen increasing from 100 L [Fig. 1(c)] to 300 L [Fig. 1(d)], more C=C and Si-Si dimers are dissociated. Consequently, the LEED pattern became increasingly more dominant with the (1×1) structure and the intensity of the $\frac{1}{2}$ diffraction points became hardly detectable. At the same time, HREELS showed that the loss peaks due to the newly formed CH_2 species increased in intensity while those associated with C_2H_2 could hardly be detected at 800-L exposure.

To probe the change of Si-H bonding in the initial stage of diamond heteroepitaxy on Si, we exposed the sample shown in Fig. 1(d) to a mixture of H_2 and CH_4 activated by the filament heated at 2200 K. Following this treatment, the LEED pattern still exhibited the (1×1) structure, but the diffraction spots became weaker and smaller while the background intensity increased. The HREELS spectrum, shown in Fig. 3(c), showed distinct changes; specifically that the intensity of the Si-H stretching vibration loss at 260 meV decreased remarkably, while that of the C-H stretching vibration loss peak at 365 meV increased a lot. One possible explanation for this change is the abstraction of the hydrogen atom from the surface Si atom and its replacement by CH_3. Of course, upon exposure to activated H_2 and CH_4, it is also possible that CH_3 and/or CH_2 adsorbs separately on Si surface. A still further possibility is that CH_3 and/or CH_2 catenated each other forming a network.

Next, we heated the sample treated as shown in Fig. 3(c) and measured the desorption products by QMS. A large amount of atomic hydrogen and a little CH_2 and CH_3 were detected when the sample was heated at 650 K. This observation showed CH_2 and CH_3 were indeed adsorbed separately and readily desorbed from the Si surface at low temperatures. However, when the heating of the sample was continued to 750 K, only H but no CH_2 or CH_3 was detected. The HREELS remained the same as that shown in Fig. 3(c), showing that hydrocarbon continued to exist on the surface. The fact that no more desorption of CH_3 or CH_2 from the Si(100) surface was observed can be interpreted to mean that the hydrocarbon species catenated each other to form a network of hydrocarbon which was difficult to desorb at 750 K. This explanation is consistent with the fact that the desorption temperature of CH_4 from Si surface is ordinarily very low.[11] We speculate that the catenation of CH_3 and/or CH_2 under the promotion of atomic hydrogen may indeed be the initial stage of diamond formation on silicon.

The present results give evidences for the several functions of atomic hydrogen that may be prevailing during CVD diamond deposition. First of all, the observation that atomic hydrogen can break up the strong C-C bonds in the adsorbed C_2H_2 and the Si-Si bonds in Si dimer leads us to believe that similar bond breakage will result irrespective of the form and bonding configuration of the adsorbed hydrocarbon on Si surfaces. The bond breaking by atomic hydrogen is a necessary step in CVD diamond growth, as it creates surface condition preferable for diamond growth on Si as well as possibly generates the necessary precursors. Second, the abstraction of H from Si-H bonds by atomic hydrogen inducing the subsequent attachment of CH_3 to Si is another necessary process created by atomic hydrogen for diamond growth on Si. Third, atomic hydrogen promotes the catenation of the chemisorbed CH_3 and/or CH_2 species to form on Si surface a network of hydrocarbon, which, in contrast to its precursor CH_3 and/or CH_2 species, is stable at an elevated temperature. Because of its high temperature stability, this hydrocarbon network is likely to survive the temperature during CVD diamond growth, and thus possibly represents the initial stage of diamond growth on Si.

IV. CONCLUSION

Atomic hydrogen was used to stimulate the formation of diamond on Si(100) surface preadsorbed of C_2H_2. This study revealed several reactions of atomic hydrogen with hydrocarbon-covered Si surface that could play a role in CVD diamond growth. Atomic hydrogen could break up the carbon-carbon bond in the adsorbed C_2H_2 and the Si-Si dimers on the Si surface, which led to the formation of C-H and Si-H bonds, respectively. When the CH_x-covered Si surface was exposed to an activated mixture of H_2/CH_4, atomic

hydrogen would abstract H from the Si-H bond and replace it with CH_x. Furthermore, under the influence of atomic hydrogen, CH_x species on Si surface would catenate to form a stable network of hydrocarbon, which possibly was the initial stage of diamond formation on Si. All three functions of atomic hydrogen are important to diamond growth on Si surfaces.

ACKNOWLEDGMENTS

This work was supported by the Strategic Grant (Project No. 7000467), City University of Hong Kong, CERG Grant (Project No. 9040144) of Research Grant Council of Hong Kong, Natural Science Foundation of China, and 863 Program of China.

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