Study on surface and interface structures of nanocrystalline silicon by scanning tunneling microscopy

Juning Gao, Haiqiang Yang, Ning Liu, Dongxia Shi, Yueshan Jiang, Zengquan Xue, and Shijin Pang
Laboratory of Vacuum Physics, Center for Condensed Matter Physics, Chinese Academy of Sciences, P.O. Box 2724, Beijing 100080, China

Yuliang He
Amorphous Physics Research Laboratory, Beijing University of Aeronautics and Astronautics, Beijing 100083, China

(Received 8 September 1996; accepted 13 May 1997)

The scanning tunneling microscope has been employed to study the morphology, atomic surface structures, and grain interface of hydrogenated nanocrystalline silicon (*nc*-Si:H) before and after hydrofluoric acid (HF) etching. It was found: (1) The *nc*-Si:H films were composed of many different sizes of grains and these grains were composed of many finer grains. (2) There were line structures on the surface of the fine grains and loop structures at the grain boundaries without HF treatment. After etching, two more structures were observed: loop structures on the surface of fine grains and spider bonding structures besides the interface of fine grains. (3) The loop structures found at the grain boundaries was larger and more irregular than those on the grain surfaces. Line structures were similar to crystal silicon, but the distance between lines was enlarged. Considering the experimental results, a discussion was made about the formation mechanism of these atomic structures. © *1997 American Vacuum Society.* [S0734-211X(97)12904-3]

I. INTRODUCTION

In the last decade, hydrogenated nanocrystalline silicon (*nc*-Si:H) films were widely used in microelectronic devices, such as thin-film transistors.[1] Recently, some researchers reported the photoluminescence of *nc*-Si:H at room temperature.[2,3] This may bring about some new applications of *nc*-Si:H. The morphology, grain size, and grain boundary of *nc*-Si:H are important characteristics for the applications of *nc*-Si:H thin films in microelectronics. The properties of *nc*-Si:H, such as electrical conductivity, are strongly influenced by the grain size and grain boundary,[4–6] so the research of the microstructures of *nc*-Si:H is essential for its applications. In the past, most research work of *nc*-Si:H was done by transmission electron microscopy, scanning electron microscopy (SEM), x-ray diffraction, and Raman spectroscopy. Recently, scanning tunneling microscopy (STM) has been used in the studies of *nc*-Si:H.[4,7] The high resolution of STM made it possible to observe surface structures from micron to atomic resolution in real space and various environments.[8] However, these air-exposed surfaces are difficult to observe because of a native oxide layer. Such an oxide layer can be removed by chemical etching in hydrofluoric acid (HF). Nakagawa *et al.* have reported the observing of Si(100) and Si(111) atomic images in air after HF treated.[9] Niwa, Iwasaki, and Hasegawa also have reported the observation of quite clear STM images for HF-dipped surfaces of Si(100).[10] However, what will happen on the surface and interface of *nc*-Si:H after HF etching has not been investigated.

In this article, STM was used to study the morphology, grain size, and grain boundary before and after HF etching, especially to observe the atomic structures of the surface and grain boundary.

II. EXPERIMENT

The *nc*-Si:H films were deposited on a glass substrate in a capacitance system of a conventional plasma-enhanced chemical vapor deposition with hydrogen (H_2) diluted silane (SiH_4) as the reactants activated by rf and dc double power sources. During the deposition process, the substrate temperature was at 300 °C, the rf power was 0.44 w/cm^2, and the total pressure of the reactive gases was 1.3–1.5 Torr. The details of the experimental parameters have been described elsewhere.[11]

The STM used in the experiment is a home-made CSTM-9000 operated in air at room temperature. The tip was from a mechanically sharpened platinum–iridium alloy wire. The STM images were taken in the constant current mode. To remove the oxidized layer, the samples were dipped into 10% HF solution for about 20 s. With the prolongation of scanning, the STM images degraded, this was due to some surface reaction caused by the tunneling current.[7,9] When the scanning area was larger than 25 nm×25 nm, the bias voltage was about 2 V and the constant tunneling current was set to about 0.5 nA. To study the atomic structure of the surface, the bias voltage and the constant tunneling current were set to 1.5 V and 1.5 nA, respectively.

III. RESULTS AND DISCUSSION

Figure 1 is a STM image of the *nc*-Si:H film. The scanning area is 50 nm×50 nm. There is a larger grain among several grains with different sizes in the image. The grain sizes measured by STM varied from 10 to 100 nm. There are

FIG. 1. STM image of *nc*-Si:H. The scale is 50 nm×50 nm.

lots of fine grains on the surface of the larger grain, and the size of the fine grain is about several nanometers. Figure 2 shows the fine grains on a larger grain. The scanning area is 25 nm×25 nm. The existence of fine grains increases the area of interfaces, so the hydrogen content increases due to the existence of a lot of Si–H bonds on the surfaces of the grains. This result can explain the high content of hydrogen in *nc*-Si:H in our previous study.[6] The existence of Si–H bonds prevented the surface from being oxidized heavily and made it possible to observe the surface and interface without HF etching.

Figures 3, 4, and 5 show the atomic structures of fine grains and their interfaces obtained after HF etching. The scanning area of Fig. 3(a) is 4.22 nm×3.14 nm. In Fig. 3 we can find two kinds of loop structures marked A and B, respectively (A: loop structure on the interface; B: loop structure on the surface). A line was drawn to cross these two kinds of loop structures and Fig. 3(b) shows the cross section along the line. Considering the morphology and the cross section, we find that A is larger and more irregular than B. Figure 4 shows another kind of atomic structure: a line structure (marked C). The scanning area was 2.61 nm×2.25 nm. The distance between two lines is about 0.45 nm, which is different from that of the crystal faces of crystal silicon. Figure 5 shows a common and interesting structure: a spider bonding structure. Also, this structure can be considered as a loop structure and many line structures instead of a new one. There is a center in the spider bonding structure, which is made up of an atom, a vacancy, or a cluster. The other atoms surrounding the center arrange themselves as a spider web.

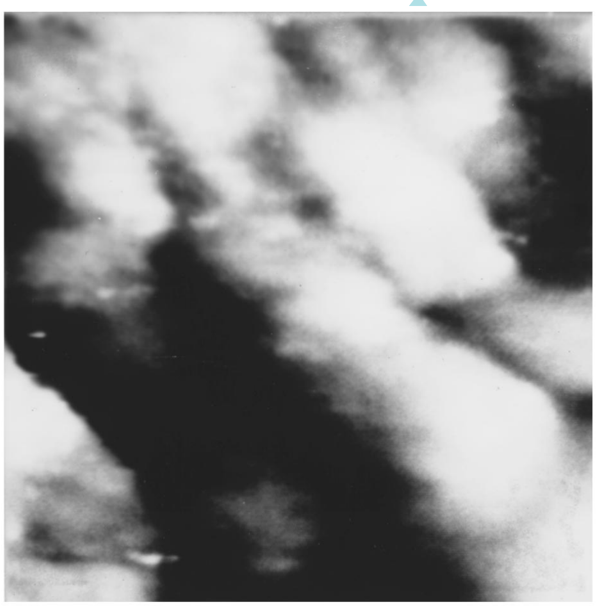

FIG. 2. STM image of fine grains. The scale is 25 nm×25 nm.

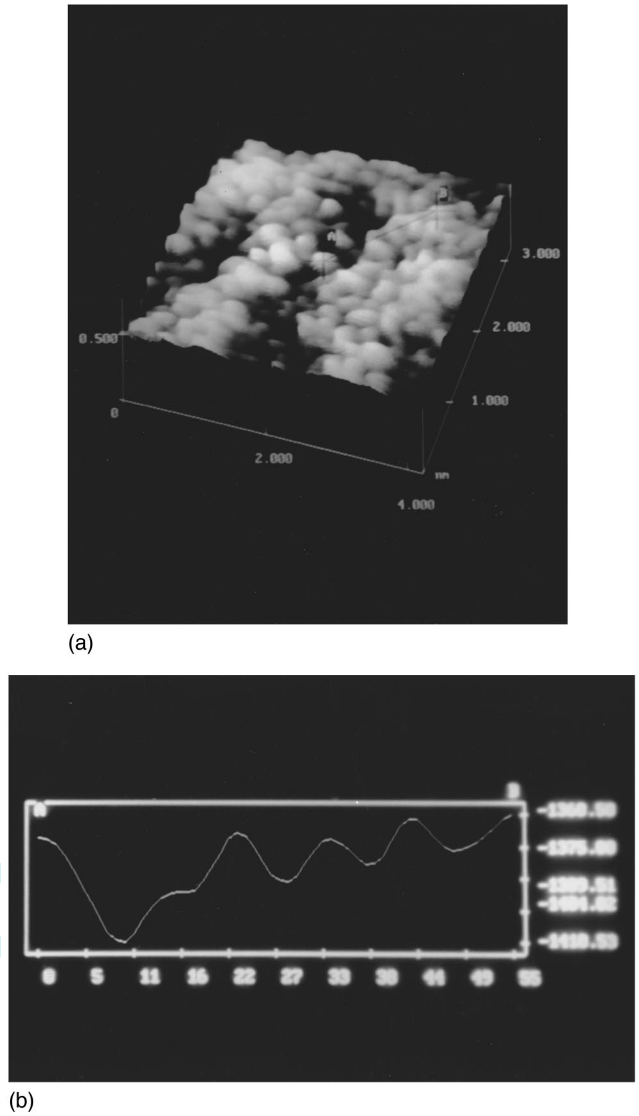

FIG. 3. (a) Two kinds of loop structures after HF etching. The scale is 4.22 nm×3.14 nm. (b) Cross section of (a). A: loop structure in the interface, and B: loop structure on the surface of the fine grain.

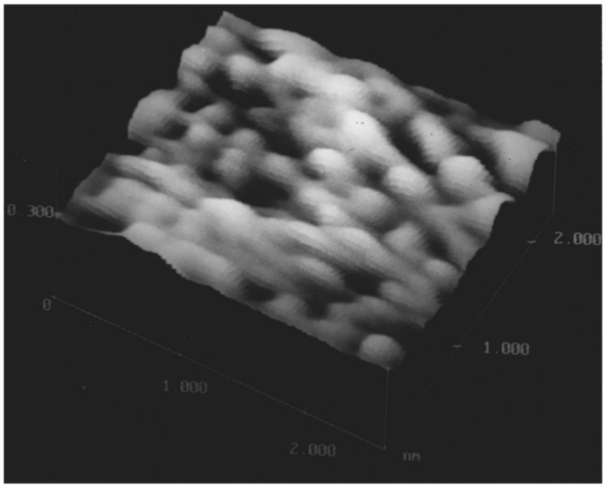

FIG. 4. Line structure (marked C) after HF etching. The scale is 2.61 nm×2.25 nm.

Etching may play a very important role in the formation of all these atomic structures. Figures 6 and 7 show STM images without HF treatment. In Fig. 6, we can find the line structure (marked D). Figure 7 shows a loop structure. Considering these different orientations around the loop, we may draw the conclusion that this loop structure is on the interface of the fine grains. Contrasted with the atomic structure after HF etching, loop structure B and the spider bonding structure are not found. This result is consistent with our previous work.[6,11] Furthermore, before HF etching, it is difficult to tell apart the single atoms from that after the HF treatment, correspondingly, even if they are a similar distance between the rows. The degradation of resolution may be caused by oxidization. On the other hand, the loop structure is very similar to loop structure A, which is obtained after HF etching.

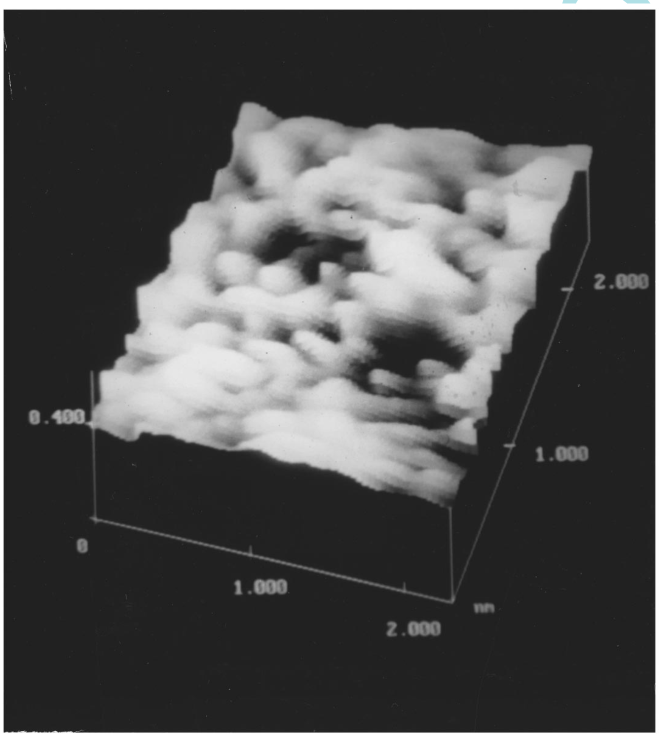

FIG. 5. Spider bonding structure beside the interface of fine grains after HF etching, 2.31 nm×2.31 nm.

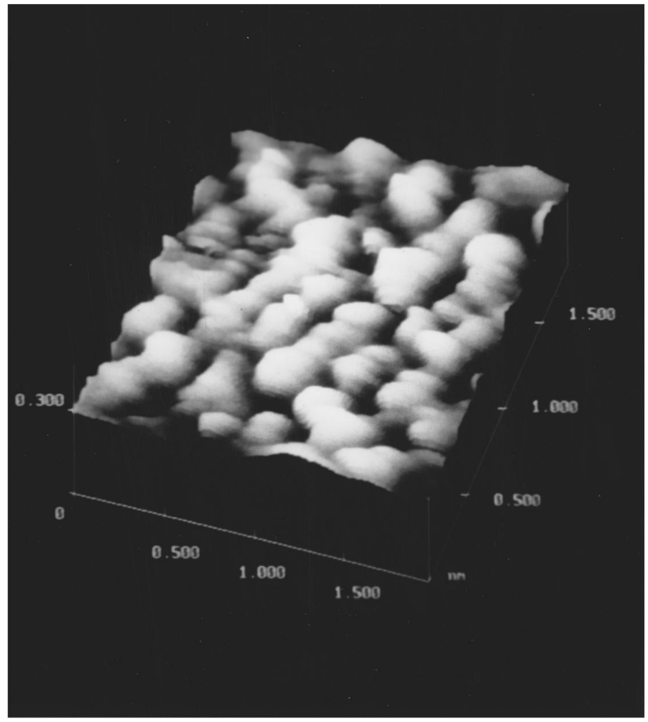

FIG. 6. Line structure in the surface without HF treatment. The scale is 1.96 nm×1.82 nm.

It is well known that an air-exposed *nc*-Si:H surface always has a native oxide layer. This layer can restrict the resolution of the images to a nanometer level.[9] While removing the oxide layer on the surface by HF etching, the bond of the silicon and the oxygen was broken. Then, dangling bonds of the silicon were produced. At the same time, many ions of hydrogen exist in the solution. In the process of the combination of atoms, the silicon atoms can combine with each other or with the hydrogen ion. On the surface of the fine grains, due to the various distances between rows of the crystal lattice, two kinds of structures, line structure and loop structure, can be formed, respectively. When the distance between the rows is close enough, to reduce the dangling bond, silicon atoms in one row would combine with the nearest atoms in the same row and those in the nearest rows. This situation would form the loop structures on the grain. To the contrary, when the distance between the rows is large, silicon atoms between the rows cannot combine. Therefore, they will combine with the hydrogen ion in the solution. So, we can find line structures on the surface. If the distance is neither too large to form the line structure nor too small to form the loop structure independently, then the loop structure and line structure will exist disordered and nonsystematic. This random collocation can be find elsewhere, i.e., in Fig. 3. In

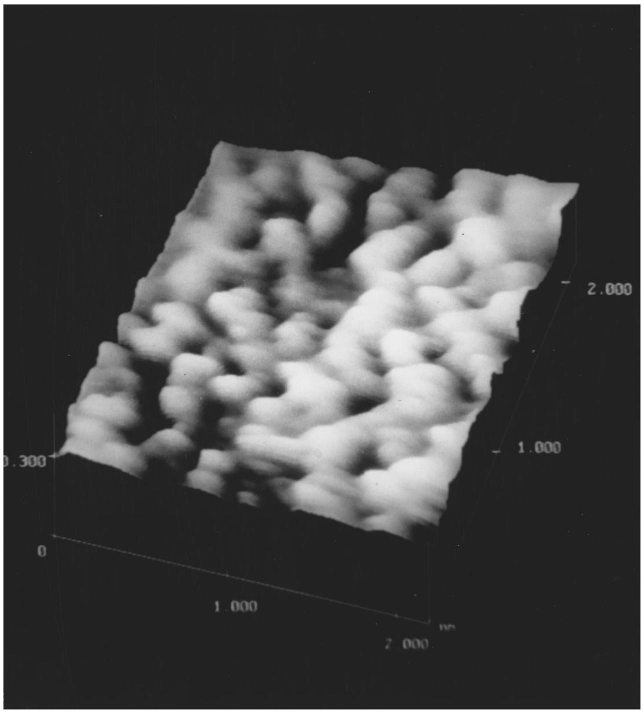

FIG. 7. Loop structure in the interface of fine grains before HF etching. The scale is 2.19 nm×2.11 nm.

comparison with the line structure, the spider bonding structure is formed near the interface. While the center atoms combine together, the other atoms have combined with the hydrogen ion as a result of the distance being enlarged. This is why the spider bonding structure can be considered as loop and line structures. Yet, we must verify that spider bonding structures are formed only beside the interface of the fine grains.

At the site of the interface, where several finer grains meet together, the loop structure on the interface can be formed. This is not because of the HF etching but because of the procedure of deposition. At the beginning of the film formation, many atoms were located and diffused on the surface of the substrate randomly. When some atoms met together, they formed a small cluster. Then the cluster as a whole grew and formed a fine grain in the end. While several fine grains met together, the larger loop structures were formed. These structures are similar to the interface model proposed by Gleiter.[5] While in etching by HF, this kind of loop structure may keep its initial form because the atoms will combine with the hydrogen ion only.

IV. CONCLUSION

The surface structures of *nc*-Si:H were studied by STM. It was found that the films were composed of many different sized grains and the grains were composed of many fine grains. Atomic images of the fine grains and their boundaries were successfully observed before and after HF etching. Three kinds of atomic structures were investigated: (1) Loop structures: After HF etching, this kind of structure was observed both on the surface of the grain and at the grain boundaries. The loop structures found at the grain boundaries were larger and more irregular than those on the surface of the grain. Consistent with Fig. 6 without HF treatment, only the loop structures on the interface can be found. We thought that the loop structures on the interface were caused by the congregation of fine grains and the loop structures on the surface were caused by HF etching. (2) Line structures: This kind of structure was similar to crystal silicon, but the distance between the lines was different. (3) Spider bonding structures: This kind of structure can only be formed beside the grain boundaries after HF etching. So, we can draw a conclusion that the etching may play a very important role in the formation process of all these atomic structures.

[1]Hong Joo Lim, Bong Yeol Ryu, and Jin Jang, Appl. Phys. Lett. **66**, 2888 (1995).
[2]Xiang-na Liu, Xiao-wei Wu, Xi-mao Bao, and Yu-liang He, Appl. Phys. Lett. **64**, 220 (1994).
[3]Hideki Tamura, Markus Ruckschloss, Thomas Wirschem, and Stan Veprek, Appl. Phys. Lett. **65**, 1537 (1994).
[4]J. K. Gimzewski, A. Humbert, D. W. Pohl, and S. Veprek, Surf. Sci. **168**, 795 (1986).
[5]H. Gleiter and Saarbrücken, Europhys. News **20**, 130 (1989).
[6]Yuling He, Chenzhong Yin, Guangxu Cheng, Luchun Wang, Xiangna Liu, and G. Y. Hu, J. Appl. Phys. **75**, 797 (1994).
[7]I. Tanaka, F. Osaka, T. Kato, Y. Katayama, S. Muramatsr, and T. Shimada, Appl. Phys. Lett. **54**, 427 (1989).
[8]G. Binning, H. Rohrer, Ch. Gerber, and E. Weibel, Phys. Rev. Lett. **49**, 57 (1982).
[9]Y. Nakagawa, A. Ishitani, T. Takahagi, H. Kuroda, H. Tokumoto, M. Ono, and K. Kajimura, J. Vac. Sci. Technol. A **8**, 262 (1990).
[10]Masaaki Niwa, Hiroshi Iwasaki, and Shigehiko Hasegawa, J. Vac. Sci. Technol. A **8**, 266 (1990).
[11]Y. L. He, X. Liu, Z. C. Wang, G. X. Cheng, L. C. Wang, and S. D. Yu, Sci. China A **36**, 248 (1993).