Microstructures of nanosize hydrogenated crystalline silicon studied by scanning tunneling microscopy

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The morphology of nanosize hydrogenated crystalline silicon (*nc*-Si:H) films have been investigated by scanning tunneling microscopy (STM) without hydrofluoric acid etching under atmospheric conditions. Images from submicrometer scale down to atomic scale have been represented. On a large scale, the *nc*-Si:H films are found to be consisted of microcrystallites separated by different interfacial regions from STM results. The mean size of microcrystallites is about 3–5 nm, which is in agreement with high-resolution electron microscopy studies. In addition, near-atomic resolution STM images provide some information on the interfacial region, which seems to be crucial for the atomic structure and many properties of nanocrystalline materials. The results show that the arrangements of the atoms on nanocrystallites are well ordered, while atoms in the interfacial regions are randomly distributed. The mechanism for imaging *nc*-Si:H is discussed.

I. INTRODUCTION

In the past ten years, polycrystalline silicon (polysilicon) thin films including *nc*-Si:H films have been widely used in integrated circuits, solar cells, and sensors. This has brought about improvements in the design and technology of these devices.[1–3] Studies of polysilicon thin films have been carried out by means of high-resolution electron microscopy (HREM), x-ray diffraction, and Raman spectroscopy.[4,5] Studies exploiting the real space, nanometer resolution capabilities of scanning tunneling microscopy (STM) and atomic force microscopy (AFM) have also been performed.[6–10] These included (1) direct observations of silicon nanocrystallites under vacuum[6] and hydrofluoric (HF) acid solution[9] to eliminate ambiguities in the STM topography caused by the presence of an oxidation layer, and (2) direct investigations of some properties such as conducting, doping, etc., on polycrystalline Si.[7–9] In addition, G. H. Wang *et al.* used STM to characterize the microstructure of nanostructured palladium and found that the nanocrystalline Pd consisted of small crystallites with an average size of about 10 nm.[11] However, direct observation of nanocrystalline materials by means of STM or AFM at near-atomic scale have not yet been carried out, especially for studies of the interfacial region, which seems to be crucial for the atomic structure and many properties of nanocrystalline materials because of its low density.[12,13]

In this article, STM and HREM are applied to *nc*-Si:H films. Images from submicrometer scale down to atomic scale of *nc*-Si:H films without HF etching in air are shown. Large scale STM images provide direct evidence of nanometer granules. Near-atomic scale STM images of *nc*-Si:H films give information on the interfacial region of *nc*-Si:H and indicate that the contrast of "crystal atoms" were enhanced compared to "interfacial region atoms."

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II. EXPERIMENT

The *nc*-Si:H films investigated in these experiments were prepared by a conventional plasma-enhanced chemical vapor deposition (PECVD) system with hydrogen-diluted silane as the reactive gas activated by RF+DC double power sources. During the process of preparation, deposition conditions must be rigorously controlled in order to form *nc*-Si:H films. A detailed description of the *nc*-Si:H film preparation has been given elsewhere.[4] The *nc*-Si:H films were directly observed at the atomic level by using a JEM-4000EX electron microscope operated at 400 kV with a point-to-point resolution of 1.9 Å, and spherical aberration coefficient, where $Cs=1$ mm. The properties of the samples were characterized using x-ray diffraction (Cu $K\alpha$, $\lambda=1.54$ Å) and Raman spectroscopy. The *nc*-Si:H materials consist of two parts: granules with size of a few to 10 nm (crystalline phase) and an interfacial region (grain boundaries and intergrain phase) separating them. The latter part has a significant influence on the properties of *nc*-Si:H materials.[4,5]

The STM images were obtained with our home-built CSTM-9000 STM operated in air at room temperature.[14,15] Tips were prepared by mechanically shearing platinum–iridium (Pt:Ir=88:12) alloy wire (0.25 mm in diameter) and electrochemically etching tungsten tips (0.25 mm in diameter). Images were performed in the constant-current mode with positive bias voltages between 0.5 and 2 V and a maximum tunneling set-point current of 1 nA. All STM images shown below are unprocessed except for smoothing of the data. Acquisition time for the 180×180 pixel images varied from 3 min (large-scale scans) to 15 s (small-scale scans).

III. RESULTS AND DISCUSSION

A series of STM topographic photographs of *nc*-Si:H films with their sizes from submicrometer scale down to atomic scale have been obtained. On the large-scale scans, STM topography of *nc*-Si:H films show individual grains.

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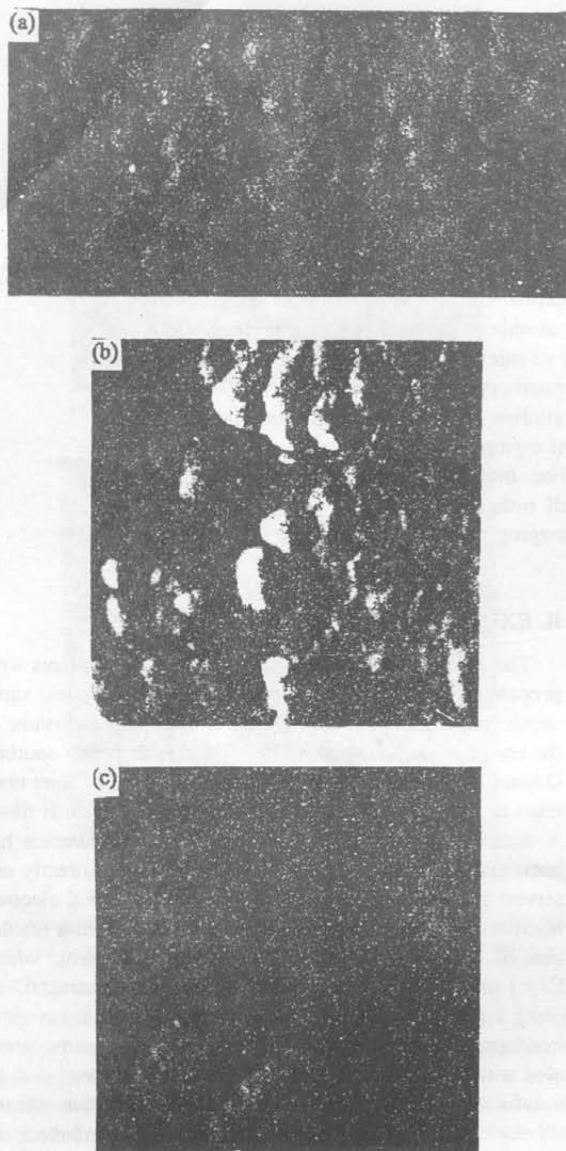

FIG. 1. Typical STM top view topographs over nanosize hydrogenated crystalline silicon films using tungsten tips obtained at a tip bias voltage of $V_t = 1.0$ V and a tunneling current of $I_{tun} = 0.45$ nA with the following field sizes: (a) 68.7×41.8 nm, (b) 40.9×48.8 nm, and (c) 20.5×24.4 nm. All images were taken in the constant current mode under atmospheric conditions.

Figure 1 shows STM top view images over the *nc*-Si:H films surface using tungsten tips obtained at a tip bias voltage of $V_t = 1.0$ V and a tunneling current of $I_{tun} = 0.45$ nA recorded with scanning areas 68.7 (*x* direction) ×41.8 nm^2 (*y* direction) [Fig. 1(a)], 40.9×48.8 nm^2 [Fig. 1(b)], and 20.5×24.4 nm^2 [Fig. 1(c)], respectively. The *nc*-Si:H surface was scanned laterally from left to right, so there is shadow in the right side of each grain. From STM topographic images in Fig. 1, some rough structures on the *nc*-Si:H films surface are clearly visible. These three images show that the *nc*-Si:H consisted of nanometer scale granules, and the number density of nanometer grains is different, among which Fig. 1(a) was revealed as closed packed, and Figs. 1(b) and 1(c) were formed loose. It showed that the local density was not uniform. STM topographic maps in Fig. 1, more clearly in Figs. 1(b) and 1(c), show that the granules are distinguished and their mean sizes are estimated to be a range of 3 to 5 nm in diameter. The sizes agree well with HREM micrographs (Fig. 2) taken on these samples.[5] The arrangement of nanocrystallites, which are separated by interfacial regions with different atomic structures, are irregular in HREM micrographs.

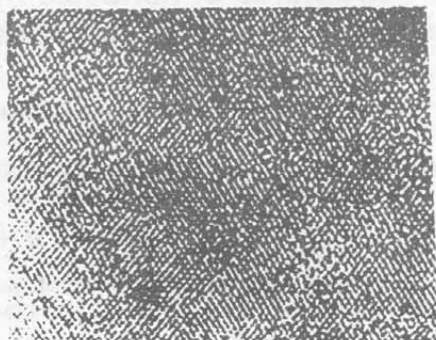

FIG. 2. A high-resolution electron microscopy image of nanosize hydrogenated crystalline silicon films.

Because STM has some advantages over HREM, additional information from Fig. 1 which could be obtained is that the interfacial region between the microcrystallites appears distinct. However, results obtained using Pt/Ir tip show that the interfacial region appeared flat due to bluntness of the tip.[16]

Depending on the sensitivity of the piezo tube, scan areas from submicrometer scale down to atomic scale could be imaged by STM. Two three-dimensional near-atomic resolution images on the *nc*-Si:H films surface, imaged via Pt/Ir tips with areas of size 4.09×4.88 nm^2 [Fig. 3(a)], 1.71×1.22 nm^2 [Fig. 3(b)], respectively, obtained at a tip bias voltage of $V_t = 1.0$ V and a tunneling current of $I_{tun} = 0.45$ nA, are displayed in Fig. 3. During a brief instability in Fig. 3(a), the probe tip may have tilted the sample. From STM images of Fig. 3(a), brighter regions represent nanometer-scale granules which are well ordered, and darker regions which are disorderly distributed represent interfacial regions. "Crystal atoms" and "interfacial region atoms" are seen in Fig. 3(a). However, "crystal atoms" are more clearly visible than "interfacial region atoms." The distance between two adjacent atoms is about 3 Å. The thickness of the interfacial region measured from Fig. 3(a) is about 1 nm, which is consistent with HREM studies. Figure 3(b) represents near-atomic resolution images on one nanocrystallite.

Gleiter *et al.* have given a model on nanocrystalline material.[12,13] Structurally, two kinds may be distinguished: "crystal atoms," the nearest neighbor configurations which correspond to the lattice configuration, and "boundary atoms" characterized by nearest neighbor configurations which

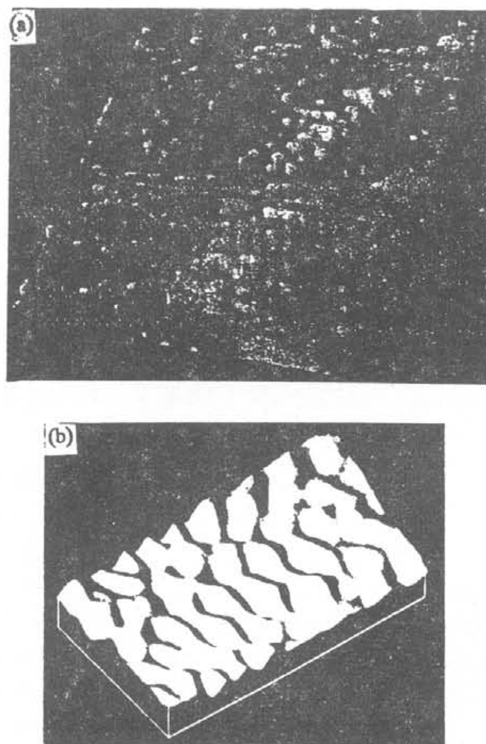

FIG. 3. Two three-dimensional near-atomic resolution images over nanosize hydrogenated crystalline silicon films with the following scanning areas: (a) 4.09×4.88 nm, and (b) 1.71×1.22 nm. All images were recorded in the constant current mode in air.

are different. Studies of the microstructures of nanocrystalline materials by means of transmission electron microscopy, x-ray diffraction, neutron diffraction, and extended x-ray absorption fine structure (EXAFS) show that crystals are separated by grain boundaries of thickness about 1 nm and density (ρ_0) some 50% of the crystal and hence considerably lower than in glasses. This low density of the boundary region seems to be crucial for the atomic structure and many properties of nanocrystalline materials. Our results confirm [from Fig. 3(a)] the model of nanocrystalline materials by direct observation for the first time.

Tanaka *et al.* reported that STM images of the HF-etched polysilicon surface became inferior during STM observation.[7] They concluded that the observed degradation of STM images was related to preferential oxidation at the grain boundary. Sugawara *et al.* used STM/AFM to investigate the polycrystalline Si surface, and also concluded that the tunneling conductance at the grain boundary decreased faster far from the grain boundary, so that the area at the grain boundary was preferentially oxidized.[10] In our STM measurements, the interfacial regions were not easy to resolve clearly. This might be caused by preferential oxidation at the interfacial region. Of course, we could not exclude that it was related to the STM imaging mechanism. This mechanism favors viewing the "ordered" surface with higher spatial resolution as well.

A voltage threshold of 0.5 to 2 V in the experiment has been found as necessary to image *nc*-Si:H films via STM. The condition was not stable below this threshold. This was caused by the presence of an oxidation layer on the *nc*-Si:H films surface. However, without HF-etched *nc*-Si:H films in our STM measurements the images still reflected the real structure of the *nc*-Si:H films surface owing to the fact that the oxidation film contributed only the potential barrier of the junction between the probe tip and sample. The STM results roughly reveal the contours of the sample surface. On the other hand, the combination of Si dangling bond and hydrogen atom would reduce the oxidation degree of the sample. These studies are just preliminary; further studies are forthcoming.

The underlying point here is that reproducible results on the *nc*-Si:H films surface have been obtained many times by STM using various tips. In addition, atom numbers increase with the enlargement of the scanning area, so these results are convincing.

IV. CONCLUSIONS

STM is a useful tool for investigating the morphology of *nc*-Si:H films from submicrometer scale down to atomic scale. We found it more convincing when it is combined with HREM. From STM images, *nc*-Si:H films are made of microcrystallite grains with a mean size of 3–5 nm. The regions between the microcrystallites appear to be distinct. Direct measurements of near-atomic images show that the arrangements of the atoms on nanocrystallites are well ordered and "interfacial region atoms" are randomly distributed. The results conform the model of nanocrystalline materials proposed by Gleiter.

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