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Scanning tunneling microscope study of microcrystalline silicon surfaces in air

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Surfaces of microcrystalline silicon films prepared by the glow discharge method have been investigated by a scanning tunneling microscope (STM) in air. Grain-like structures of 30–80 nm size which correspond to transmission electron microscope data have been observed. The film surface was found to be geometrically rather flat but the structure was observed electrically, that is, the resistivity seemed to be inhomogeneous due to preferential oxidation. Also, degradation of STM images of a HF-etched microcrystalline silicon surface has been observed for the first time.

Microcrystalline silicon films are a promising material for application in electronic devices with large areas, for example, solar cells and thin-film transistor arrays.[1,2] These devices generally are multilayered structures, so that their structural and electronic surface characteristics of morphology and degree of oxidation are important factors in their performance. Nevertheless, before the advent of the scanning tunneling microscope (STM), it was difficult to characterize nonperiodic or disordered surfaces such as that of microcrystalline silicon films with nanometer scale resolution in real space.

The STM has made it possible for us to observe surfaces with submicron to atomic resolution in real space in various environments.[3,4] Its high resolution even in a laboratory atmosphere makes it potentially useful for investigation of various semiconductor processes like thin-film deposition, epitaxy, and etching. Gimzewski *et al.* first investigated the surface of nanocrystalline silicon film by STM under a vacuum of 10^{-6} Pa and observed 10 nm order structures which were apparently granular.[5]

In this letter, we report the study of surface morphology of microcrystalline silicon films prepared by the glow discharge method by scanning tunneling microscope in atmosphere during which we observed 30–80 nm grain-like structures. The film surface seemed to be geometrically rather flat and the structure was observed electrically probably because the surface had an inhomogeneous electric resistance due to oxidation.

Results of STM observation are discussed in comparison with the data obtained from a transmission electron microscope (TEM) photograph.

n-type microcrystalline silicon films were prepared by rf (13.56 MHz) glow discharge decomposition of a monosilane (SiH_4), phosphine (PH_3), and hydrogen (H_2) mixture in a capacitively coupled diode system. The films were grown to 0.1–0.2 μm thickness on Corning 7059 glass substrates and had *n*-type conductivity of 1.0 $\Omega^{-1}\,cm^{-1}$. The substrate temperature, chamber pressure, and rf power density were 230 °C, 80 Pa, and 0.4 W/cm^2, respectively.

One sample was cut into three pieces. One piece was observed by STM without further processing. A thin (4 nm thick) gold film was evaporated on the second piece by a conventional vacuum evaporator to eliminate electric information from STM data and to provide only geometric information. The last piece was HF etched to remove the native oxide from the microcrystalline silicon surface. The etching was made with 4.5% HF aqueous solution at room temperature for 30 s.

The STM system we used has a stepper motor for fine positioning of the tip on the surface and a piezoelectric tube scanner for topographic measurements. A Pt-Ir alloy tip was used in this study. For as-deposited and HF-etched surfaces, STM data were taken with the following conditions: constant tunneling current of $I = 2$ nA, bias voltage of $V_b = 2$–4 V (tip positive), and scanning rate of $f = 5$ Hz. It was impossible to obtain a stable STM image with $V_b < 1.5$ V. For the gold-evaporated surface, $V_b = 50$ mV was used while other conditions remained the same.

Figure 1 shows a typical STM image of an as-deposited microcrystalline silicon surface. Granular structures 30–80 nm wide and 5–10 nm high are clearly seen.

STM images generally contain both geometric and electronic information. In order to obtain geometric information only, we examined the gold-evaporated sample, the surface of which shows a larger and smoother topographic pattern (Fig. 2).

Examination of the gold-evaporated surface revealed a geometric pattern size of microcrystalline silicon film which

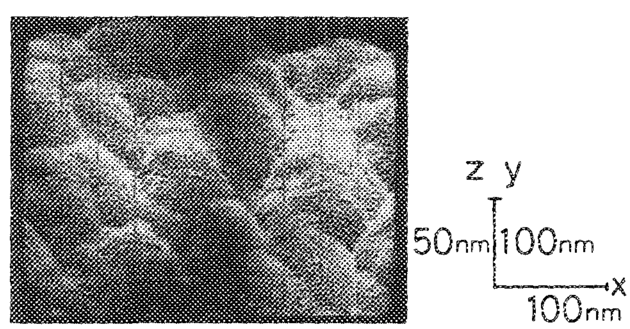

FIG. 1. STM image of as-deposited microcrystalline silicon surface.

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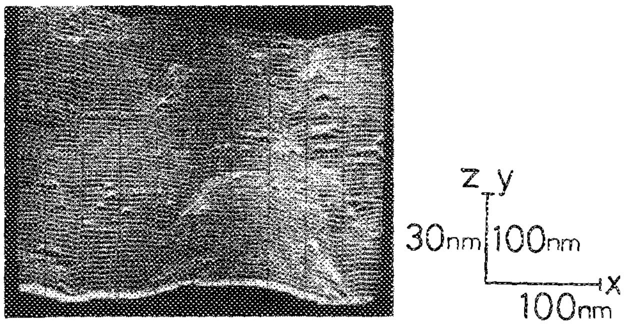

FIG. 2. STM image of gold-evaporated microcrystalline silicon surface.

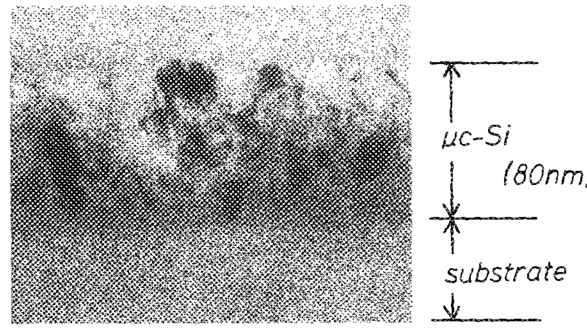

FIG. 4. Cross-sectional TEM image of microcrystalline silicon film.

seemed larger than the characteristic size of the granular structure in Fig. 1. Thus, the structure in Fig. 1 reflects electric information, that is, the electric resistance is not uniform throughout the microcrystalline silicon surface. Since STM images of the HF-etched surface show a large topographic pattern similar to the gold-evaporated surface (Fig. 3), inhomogeneous oxidation seems the probable cause of the resistance variation on the surface.

Because the TEM photograph of a sample prepared by a similar process (Fig. 4) shows grains of comparable size with our STM data (Fig. 1), this inhomogeneity may reflect the micrograin structure. At the grain boundary, the resistance could be higher than that of the crystallized region because of preferential oxidation and the microcrystalline boundary may be observed not geometrically but electrically.

Gimzewski *et al.* investigated the surface of a nanocrystalline silicon film under a vacuum of 10^{-6} Pa and observed 10 nm order structures geometrically which they interpreted as individual grains because they had the same characteristic size as that of a TEM lattice image.

It would be possible to observe the micrograin boundaries electrically when they are preferentially oxidized, although it seems difficult to observe them geometrically in atmosphere.

Another interesting fact is that the images of the HF-etched microcrystalline silicon surface became inferior during STM observation. Photographs in Fig. 5 show a gradual increase in the noise with scanning. This phenomenon is believed to be due to some surface reaction caused by tunneling current because when the tip was moved to another place a clear image was restored, which was then again followed by rapid degradation. This demonstrates one possible STM application for nanometer scale processing.

This degradation of images was not seen in HF-etched amorphous silicon which was grown by a similar glow discharge process. Thus, the observed degradation of STM images is related to the microcrystalline boundary.

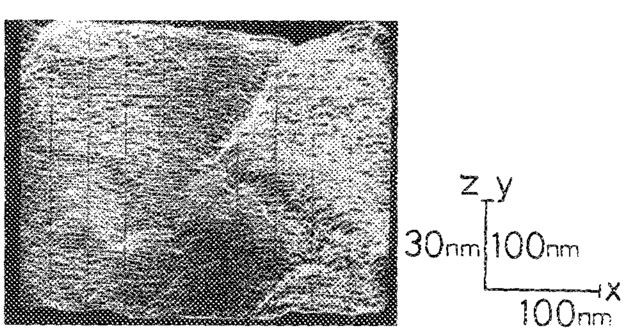

FIG. 3. STM image of HF-etched microcrystalline silicon surface.

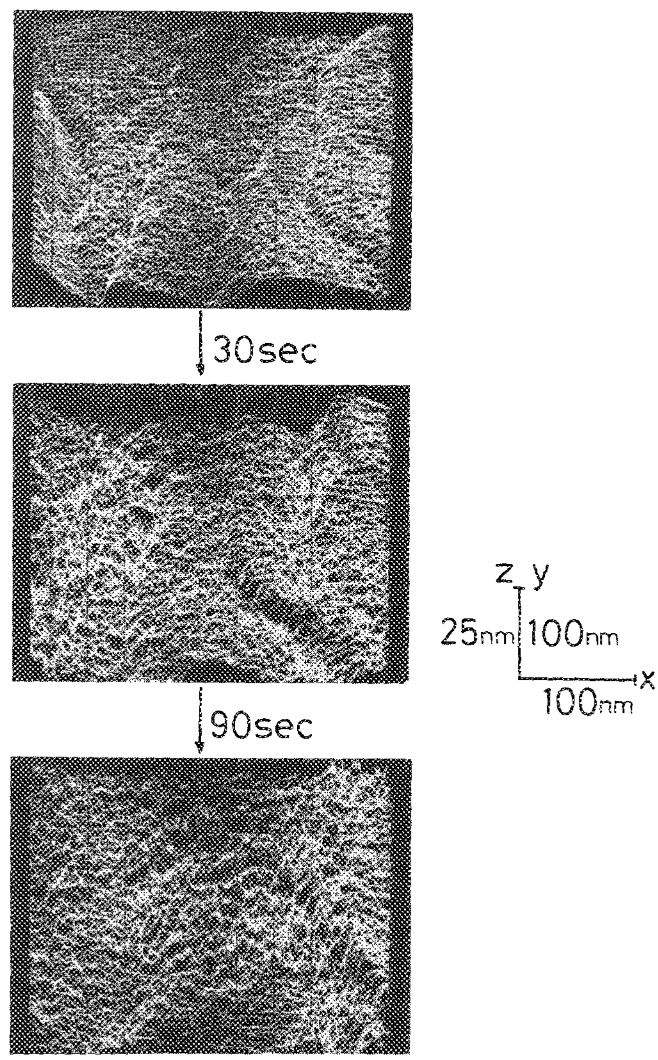

FIG. 5. Degradation of STM image by tunneling current.

Microcrystalline silicon surfaces have been investigated by STM in air. A surface topographic pattern which has the same characteristic size as that of a TEM image was observed on the as-deposited film surface. Since gold-evaporated and HF-etched sample surfaces show larger topographic patterns, not only geometric but also electric properties contribute to STM images probably through oxidation at the grain boundary. Namely, the microcrystalline silicon film surface seems to be rather smooth but inhomogeneously oxidized.

Degradation of STM images of a HF-etched microcrystalline silicon surface has been observed for the first time. This is an interesting phenomenon from the viewpoint of nanometer scale processing.

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