Control of the Formation Dynamics of Nano-Clusters of Iodine Compounds on an H-Terminated Si(111) Surface in a Concentrated HI Solution

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INTRODUCTION

Formation of regulated nano-structures on semiconductor surfaces constitutes the basis of future hugely integrated and intelligent devices. A number of studies have been reported on spontaneous formation of aligned nano-structures of metals or semiconductors on solid surfaces by deposition under ultrahigh vacuum (UHV) conditions. On the other hand, little is known on spontaneous formation of ordered nanostructures at the solid/solution interface, except for the formation of nano-rods or dots by making use of appropriate templates.

Recently we discovered some unique examples of spontaneous formation of ordered nano-structures at the solid/solution interfaces[1-5]. These are of great interest in view of exploration of the self-organizing ability of molecular systems and its development to nanotechnology. In the present work, we have made detailed studies on the formation of oriented nano-rods on the H-Si(111) surfaces when they were immersed in 7.6 M HI, with an emphasis placed on the elucidation of the growth mechanism. The investigation of the effect of the immersion temperature has revealed that the size and shape of clusters and hence the growth mechanism drastically change with the immersion temperature.

EXPERIMENTAL

H-Si(111) surfaces were obtained by the conventional RCA cleaning method, followed by etching with 5% HF and 40% NH_4F. The Si surface thus treated was then immersed in temperature controlled 7.6 M HI for certain periods of time. Surface morphology was inspected by tapping-mode atomic force microscopy (AFM) in air. The amount of adsorbed iodine on the surface was monitored by X-ray photoelectron spectroscopy (XPS) (Si-2p, I-3d) spectra. Si-H bonds and surface oxidation were studied by in-situ multiple internal total reflection Fourier transform infrared spectroscopy (FT-IR).

RESULTS & DISCUSSION

Figure 1 shows AFM images of H-Si(111) surfaces (a) before and (b)-(d) after immersion in 7.6 M HI, where the temperature of the HI solution is changed from (b) 5˚C to (c) 63˚C and (d) 81˚C. The scale-like pattern in Figure 1(a) represents a step and terrace structure of the H-Si(111) surface. For the immersion in 7.6 M HI at 5˚C for 480 min (Figure 1b), a number of long rod clusters are formed everywhere on the Si(111) surface. The AFM inspection showed that the width, height, and length of the rod clusters were about 20 nm, 1~2 nm, and 100~200 nm, respectively. It is to be noted also that the rods show a high degree of alignment, that is, they are all aligned in the direction or equivalents of the Si(111) surface. For the immersion at a slightly higher temperature of 63˚C for 240 min (Figure 1c), on the other hand, not the rods but dot clusters were formed at terraces and steps of the Si(111) surface. For the immersion at a further high temperature of 81˚C for 60 min (Figure 1d), dot clusters were also formed, but their size and shape were quite different from those in Figure 1(c). We can roughly say that the dot clusters in (c) are small and round, the diameter and height being about 20 nm and 10-15 nm, respectively, whereas the dot clusters in (d) are large and flat, the diameter and height lying about 100 nm and 1 nm, respectively. In order to investigate the growth mechanism in more detail, we inspected a change in the size and shape of the clusters with the immersion time. Those results strongly suggested that the formation of the dot clusters at a high temperature is controlled by thermodynamics, whereas that of the rod clusters at a low temperature is controlled by kinetics.

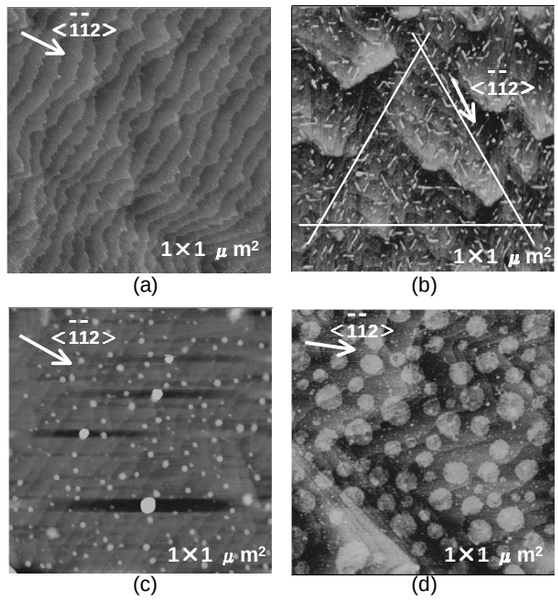

Figure 1 AFM images for H-Si(111) surfaces (a) before and (b)~(d) after immersion in 7.6 M HI. The immersion time and temperature are (b) 480 min, 5˚C, (c) 240 min, 63˚C, and (d) 60 min, 81˚C. White lines forming a triangle, added to (b), indicate the direction and equivalents of the Si(111) surface.

CONCLUSION

The formation of nano-sized clusters on nearly atomically-flat, H-terminated Si(111) surfaces, when immersed in 7.6 M HI in a temperature range of 5 to 81˚C, was investigated by AFM, XPS, and FTIR observations. AFM inspection has revealed that long rod clusters, aligned in the directions of the threefold symmetry of the Si(111) surface, are formed in the immersion temperature below about 30˚C, whereas circular dot clusters were formed in the immersion temperature above 30˚C. It is discussed that the formation of the oriented rod clusters at a low temperature is caused by a diffusion-controlled mechanism, whereas that of the dot clusters is caused by a thermodynamics-based mechanism.

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