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High resolution scanning tunneling microscope observation of Si nanoparticles fabricated by laser ablation and sparsely deposited on HOPG

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High resolution scanning tunneling microscope observations on Si nanoparticles fabricated by the laser ablation method and deposited on HOPG substrates, revealed that there exists many irregular projections and depressions all around the surface of the Si nanoparticles . As a result, the outward appearance of the Si nanoparticles resembles a cluster of grapes. In some cases, a $\sqrt{3}\times\sqrt{3}$ superlattice structure was observed in the vicinity of the Si nanoparticles which might indicate that some of the Si nanoparticles are partly buried in the HOPG substrate.
Key words: Si nanoparticles, scanning tunneling microscope, laser ablation, HOPG

1. INTRODUCTION

Since the discovery of visible light emission from small silicon structures in anodically etched porous silicon (PS) layers at room temperature [1], a great deal of research has been devoted to investigate the characteristics, light emission mechanism, and topography of Si nanostructures with an anticipation that they might serve as a material to fabricate novel optoelectronic devices [2]. It is generally believed that the quantum confinement effect in these Si nanostructures plays an important role to modify the energy gap of the indirect band gap Si semiconductor to a direct semiconductor so that visible light is produced as experimentally observed [2]. In addition, it is known that the surface structure of the Si nanoparticles seriously influence the optical characteristics [3]. In this sense, in order to understand the still debated light emission mechanism, it is important to establish a method to fabricate well characterized Si nanoparticles and to observe their topographies with probes which has high spatial resolution such as scanning tunneling microscope (STM). Information obtained from these observations might yield a good feedback for the fabrication methods in order to optimize the experimental conditions and improve the quality and uniformity of the Si nanoparticle layers.

Several STM and atomic force microscopy observations have been implemented to investigate the morphology of the electrochemically anodized PS layers [3-6]. Tao Yu *et al* have observed the surface morphology of PS layers observing pores and hillocks down to 1-2 nm size, showing that their shape and distribution on the sample surface is influenced by crystallographic effects [4]. Several other STM observations have been reported by other groups, though the resolution was not enough to observe the details of the surface structure of the nanoparticles [4-8]. In addition, there exists a serious limitations in researches of the electrochemically anodized PS layers because the structure of the PS layers is like a spongy body, thus it is difficult to know which part of the body contributes to the photoluminescence process. In this sense, it is necessary to fabricate isolated Si nanoparticles and observe their morphology to directly connect the topography of the Si nanoparticles to their optical characteristics.

Pulsed laser ablation is an ideal method to fabricate well characterized and isolated Si nanoparticles with uniform quantities [8-12]. Even though the underlying ablation process is complex and difficult to control, the basic concept of pulsed laser ablation is simple. A pulsed laser beam is focused onto a Si wafer target placed in a chamber filled with inert gas. Plasma forms and Si nanoparticles are made as a result of collisions of the hot Si atoms with the inert gas. By placing a

substrate at proper positions, it is possible to sparsely deposit isolated Si nanoparticles on the substrate. These samples would be ideally suited to investigate the unknown details of the surface structure of the Si nanoparticles. Implicitly, it is assumed that the shape of the Si nanoparticles are close to a complete sphere, and that the shape and size do not depend on the deposited position for a sample with typical sizes, e.g., 1 cm × 1 cm.

In this article we report on a high resolution STM observations of isolated Si nanoparticles sparsely deposited on HOPG substrates. We show that on the surface of Si nanoparticles there exist numerous irregular projections and depressions all around the surface, and as a result, their outward appearance resembles a cluster of grapes. In some cases, the $\sqrt{3}\times\sqrt{3}$ superlattice structure was observed in the vicinity of the Si nanoparticles which might indicate that some of the Si nanoparticles are partly buried in the HOPG substrate.

2. EXPERIMENTAL

A schematic of the ablation chamber is shown in Fig. 1. A Si wafer was placed at the focal point of the laser beam. The chamber was evacuated to 2×10^{-6} Torr, and after that filled with Ar gas, with a pressure ranging from 2 to 10 Torr. A predetermined number (typically 50) of single YAG pulsed laser shots (10 nsec, 25 mJ) were focused and irradiated to the target Si wafer with an interval of approximately 1 sec. Si nanoparticles formed by collision of the hot Si

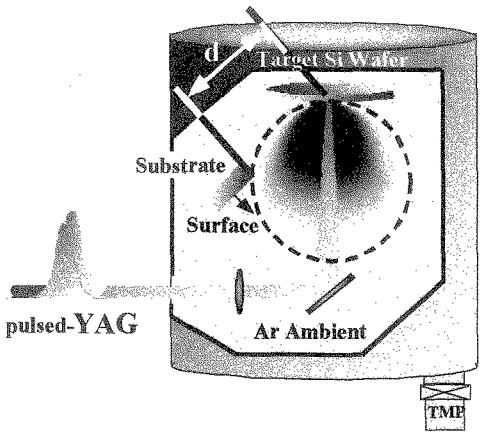

FIG. 1. A schematic of the laser ablation instrument.

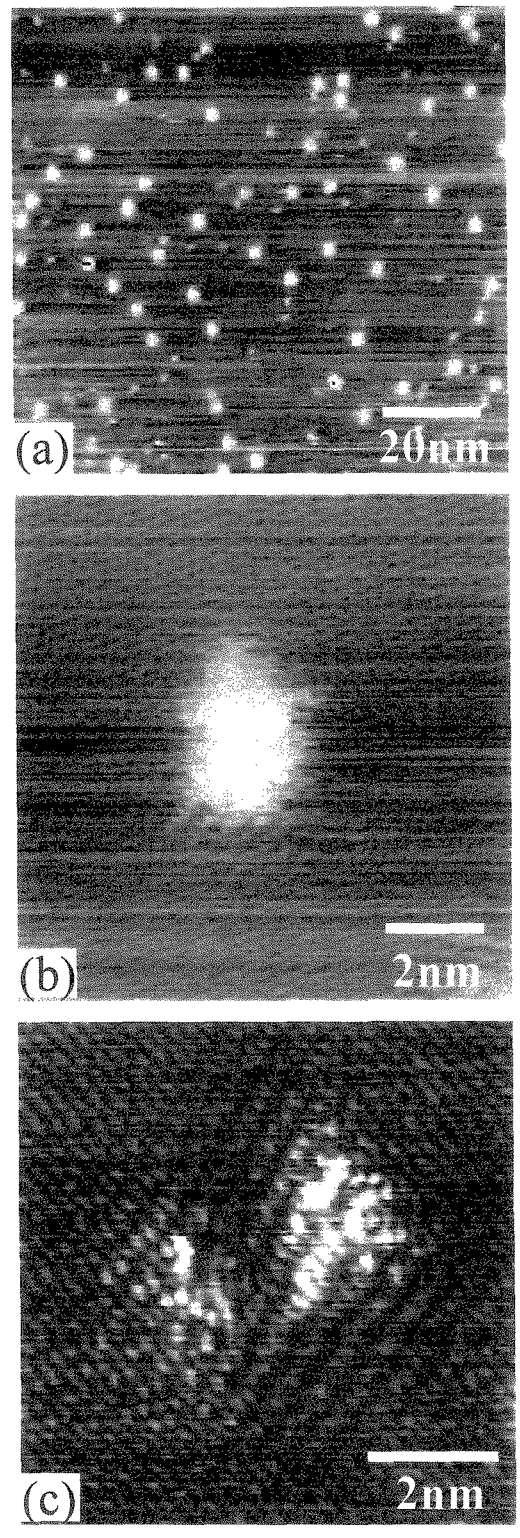

FIG. 2. (a) A typical STM image of the Si nanoparticles deposited on HOPG. (b) A high resolution STM image showing the details of the surface morphology. (c) A Si nanoparticle surrounded by a superlattice structure.

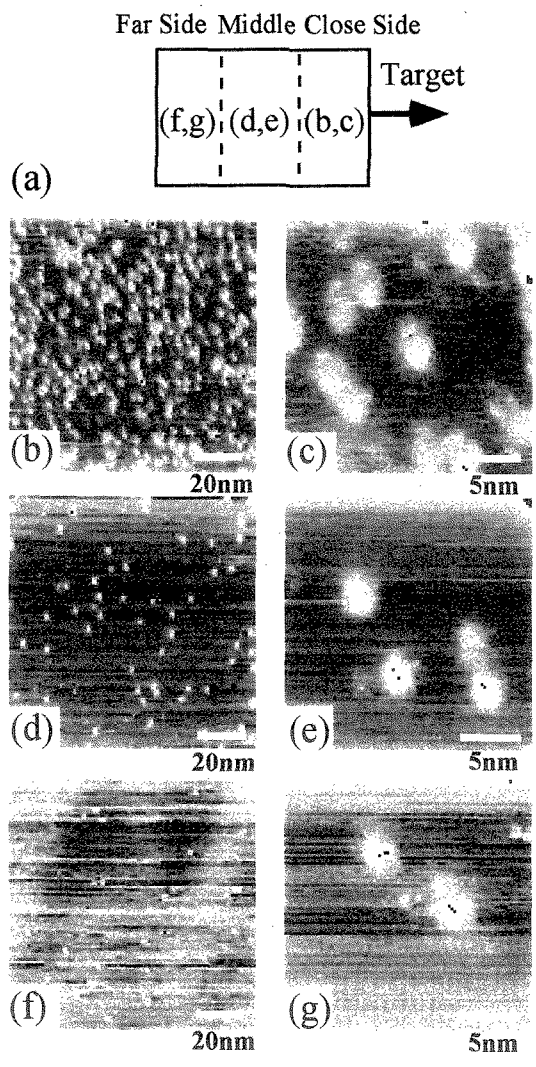

FIG. 3. A set of STM images taken at different locations of the HOPG substrate (both sides and the middle) as indicated in the schematic in (a).

atoms in the plasma with the inert gas softly lands on a freshly cleaved HOPG substrate. Due to some unknown effects, the dependence of the density of the nanoparticles on the shot number was not substantial (above 50). The HOPG substrate was glued to a copper sheet which itself was attached to a copper base. The HOPG surface was placed with an orientation angle of approximately 45 degrees from the target wafer and the typical distance from the focal point of the laser is around −10 to 15 mm. The cleaved HOPG surface was faced away from the target Si wafer to ensure soft landing of the nanoparticles to the substrate. The base pressure of the Ar gas is an important experimental parameter by which the mean size of the Si nanoparticles can be controlled. However, in this study we concentrate on results obtained with a base pressure of 5 Torr as we found that larger nanoparticles are easily disturbed by the scanning of STM and finally swept away. With these experimental conditions, we succeeded in fabricating samples with isolated Si nanoparticles with the size of 2 to 5 nm sparsely deposited on the HOPG substrate. The HOPG substrate was taken out in air after the ablation process, and as a result their surface layers are oxidized. STM measurements were carried out as fast as possible.

3. RESULTS AND DISCUSSION

Figure 2(a) shows a typical STM image (100 nm x 100 nm) of the HOPG substrate with Si nanoparticles sparsely deposited on it. It can been seen that each of the Si nanoparticles are isolated quite well and that the Si nanoparticles are distributed randomly. This implies that the Si nanoparticles are deposited at the position they hit the surface and do not migrate. At this scale, which is similar to that of previous researches, the shape of the Si nanoparticles resembles a neat circle. A close up STM image of a Si nanoparticle deposited on HOPG is shown in Fig. 2(b). From Fig. 2(b), it can be seen that the shape of the Si nanoparticle is not a complete circle, and there exists some irregularity in shape. The degree of the irregularity in shape strongly varies from particle to particle. The details of the surface morphology of the Si nanoparticles show small irregular projections and depressions all around the surface, and as a result, their outward appearance resembles a cluster of grapes. It is not clear, at this stage, whether or not this irregularity in the surface morphology reflects topographical irregularity of the Si core (if they exist) which is observed as a complete sphere in transmission electron microscope images [12], or is induced by the irregularity in the oxidized surface layer. It should be noted that almost all of the Si nanoparticles (several thousands) we observed fabricated with various experimental conditions showed this small irregularity in its surface morphology. In some particular cases, we observed a local $\sqrt{3}\times\sqrt{3}$ superlattice structure on the HOPG substrate in the vicinity of the Si nanoparticles as displayed in Fig. 2(c). Local $\sqrt{3}\times\sqrt{3}$ superlattice structures are commonly observed in the vicinity of defects, which origin is ascribed to long range electronic perturbations caused by the defects [13]. In some cases these defects are assumed to lie just below the surface

layer [13]. The existence of the superlattice might imply that the lower part of some of the nanoparticles are buried in the HOPG substrate.

Several observations carried out on different locations of the HOPG substrate (6 mm × 6 mm) revealed that the density of the deposited Si nanoparticle strongly depends on the distance from the focal point of the laser at the target Si wafer, where a closer distance gives a larger density of particles, as shown in a set of STM images displayed in Fig. 3. Figure 3(a) shows a schematic of the HOPG substrate in which we indicate the locations where the STM images in Fig. 3 were taken with corresponding printed letters. Figs. 3(b) and (c) were taken at the close side, Figs. 3(d) and (e) at the middle, and Figs. 3(f) and (g) at the far side of the HOPG substrate. Immediately it is clear that the density of the nanoparticles decreases as the distance from the focal point at the Si target wafer increases. However, when we carefully look at each Si nanoparticles taken at different positions (typical examples displayed in Figs. 3(c), (e), (g)), we notice that the size and shape of the nanoparticles are very similar (the mean size might slightly decrease at the far side). At the very first look, the nanoparticles in Fig. 3(b) and those in the other Figures appears different, though a close inspection reveals that the large structures observed in Fig. 3(b) are aggregations of nanoparticles observed in the other images. Therefore, the density of the Si nanoparticles strongly depend on the distance from the focal point, though the shape and size of the individual nanoparticles are almost independent. This result suggests that the formation process of the nanoparticles is completed before they reach and absorb on the HOPG substrate, and excludes nucleation and growth as the formation process of the nanoparticles.

4. CONCLUSION

In conclusion, we carried out an STM observation of oxidized Si nanoparticles fabricated by the laser ablation method and sparsely deposited on HOPG. High resolution STM images revealed the details of the surface morphology of the nanoparticles. Most of the observed nanoparticles had many irregular projections and depressions all around the surface, and as a result, their outward appearance resembles a cluster of grapes. In some cases, a local $\sqrt{3}\times\sqrt{3}$ superlattice structure was observed on the HOPG substrate in the vicinity of the nanoparticles which might suggest that the lower portion of these nanoparticles are buried in the HOPG substrate.

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