Surface Droplet Epitaxy for Fabrication of Metal/Semiconductor Bilayer Dots on Nanometer Scale

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(Received: 15 January 1998; Accepted: 4 March 1998)

Abstract

A new technique for the fabrication of a heteromaterial junction on a nanometer scale was investigated. Nanoparticles of gold and silver were used as a transport medium for liquid phase epitaxial growth of silicon. As a result, metal/Si bilayer dots were formed on the surface of the Si substrates. On the basis of a structural and an elemental analysis using a transmission electron microscope and energy-dispersive X-ray spectroscopy, we describe the formation kinetics of the metal/semiconductor heterojunction. This process is based on the self-assembly process and is called "surface droplet epitaxy (SDE)". Additionally, the characteristic structure of bilayer dot, i.e., the epitaxial relation between metal particles and the Si dot with large expansion of the lattice constant of metal particles, is attributed to a size effect of nanoscale materials.

1. Introduction

The main purpose of this study is to investigate a new technique for the fabrication of metal/semiconductor heterojunctions on a nanometer scale. A self-assembly technique is applied for this purpose, in which alloying and phase separation between metal nanoparticles and the surface layer of the Si substrate took place through thermal annealing and cooling processes.

Downsizing of the elemental dimensions of semiconductor devices has been achieved over the last few decades. The development of lithographic techniques has been the leading cause of this improvement [1]-[3]. As a result, very fine patterning has been achieved, even on a submicron order. On the other hand, quantum-size devices, such as a light emitting devices [4] and a single-electron devices [5], have attracted much attention because of their outstanding properties. However, they are even smaller than 10 nm in size and are beyond the formation ability of conventional lithographic techniques. Therefore, the demand for new techniques of material design on a nanometer scale has been increasing.

Recently, an initial stage of epitaxial thin film growth has been applied to the fabrication of nanoscale materials. In the growth mechanism such as the Stranski-Krastanov (SK) mode or Volmer-Weber (VW) mode, 3-dimensional island growth takes place and enables to nanoscale hemispheric dots be obtained on the substrates. Because these processes do not involve any conventional patterning tech-niques, they are called 'self-assembly processes' and are mainly applied to compound semicon-ductors [6]-[9]. For further improvement of these materials design techniques, the fabrication of a heteromaterial junction, for example, between metal and semiconductor, is a crucial issue.

In this work, we demonstrate the self-assembly technique for the fabrication of a metal/Si heterojunction. Our concept is based on assembling nanometer-scale materials instead of the conventional idea of patterning large-scale materials. Fine metal particles with nanometer-order diameter were generated by gas-condensation method and deposited on a Si substrate. Due to alloying and phase separation which occurred between the Si substrate and the fine metal particles, a bilayer dot structure could be fabricated on a nanometer scale.

2. Experimental

Single-crystalline Si substrates oriented to the (111) lattice plane were used in this study. These were chemically cleaned and dipped in HF solution (2 wt.%) for 20sec to remove the oxide layer and to terminate the surface with hydrogen atoms. The substrates were mounted into a vacuum chamber for metal particle deposition.

Gold and silver (99.99%) were evaporated by resistance heating from alumina crucibles in vacuum chamber with a background pressure of 1×10^{-6} Torr. Then, Ar gas was introduced into the chamber to produce the fine metal

particles; this is the gas-condensation method. The size of the metal nanoparticles, which were deposited on the Si substrates at room temperature, was controlled by changing the Ar gas pressure from 1 to 10 Torr.

The specimens thus prepared were then mounted into a high-vacuum chamber with a background pressure of less than $1x10^{-8}$ Torr for heat treatment. The specimens were thermally annealed for 30 min at 800℃ for gold and at 950℃ for silver. In the two cases, the temperature was elevated at the rate of 15 ℃/min and gradually cooled at the rate of -2 ℃/min to room temperature, respectively. The experimental geometry and procedures are illustrated in Fig.1.

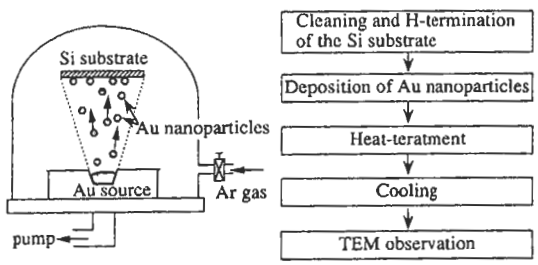
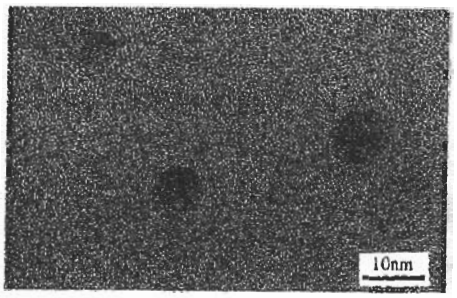


Fig.1 Experimental geometry and procedure. The metal nanoparticles were generated in Ar atmosphere and deposited on the hydrogen-terminated Si surface. Bilayer dots were fabricated through thermal annealing and cooling in high vacuum.

The structural and elemental analyses were carried out using a high-resolution transmission electron microscope (HRTEM, JEOL-2010) with energy-dispersive X-ray spectroscopy (EDX, Oxford-Link ISIS).

3. Results and discussion

Figure 2(a) shows a TEM image of the Au nanoparticles of about 10 nm in diameter which were generated at the Ar pressure of 6 Torr and deposited onto a carbon film for TEM observation. Figure 2(b) shows a cross-sectional TEM image of a post-annealed specimen, observed from the [11$\bar{2}$] direction. This image indicates that a mushroom-shaped bilayer dot was grown on the completely flat surface of the Si substrate. The EDX elemental analysis revealed that the top hemispheric layer consisted predominantly of Au with a small amount of Si, whereas the lower truncated-cone layer contained only Si [10], [11].



(a) Au nanoparticles

(b) Mushroom-like Si/Au bilayer dot

Fig.2 (a) Au nanoparticles produced at the Ar pressure of 6 Torr. (b) Cross-sectional TEM image of post-annealed specimen, viewed from the [11$\bar{2}$] direction, indicating epitaxial growth of Si dot and Au nanoparticle.

Furthermore, the lower Si dot was found to have the same crystal orientation as that of the Si substrate. Although the lattice image indicates a small tilt relative to the orientation of the Si dot, the top Au particle also can be inferred to have an epitaxial relation with the Si dot and the substrate. This epitaxial relation of the Au particles seems to be dependent on their size; the smaller Au particles tend to indicate the same crystal orientation. In contrast, the crystal orientation of the lower Si dot consistently coincides with that of the substrate, regardless of the size of the Au particles.

On the basis of these experimental results, we deduce the kinetics of the bilayer dot formation as follows. First, the hydrogen atoms terminating the Si surface are removed at above 400℃ [12]. Then, the Si atoms can easily diffuse on the clean surface at the annealing temperature. Second, they are incorporated into the Au nanoparticles and form the SiAu alloy. Because the annealing temperature is much higher than the eutectic temperature of the Si-Au binary system, 364 ℃, the alloy is considered to form a liquid phase droplet. Third, the Si atoms are precipitated from the alloy and regrown epitaxially on the substrate during the cooling process. As precipitation proceeds, the size of

the alloy becomes small. This is the reason why the Si dot shaped like a truncated cone. Finally, Si and Au separate, leaving a small amount of Si in the Au particle at room temperature. Namely, this process is a kind of liquid phase epitaxy (LPE) in which gold is used as a transport medium for Si growth [13], [14].

Koguchi *et al.* have succeeded to form quantum-dots of compound semiconductors from liquid phase nanoparticle and named the process 'droplet epitaxy' [15]. We also utilized nanoscale droplets for the purpose. In our case, the surface diffusing Si atoms play a key roll for the formation of SiAu alloy droplets and lead to the fabrication of the metal/ semiconductor heterojunction. Consequently, we call this process "surface droplet epitaxy (SDE)" , and it is schematically illustrated in Fig. 3.

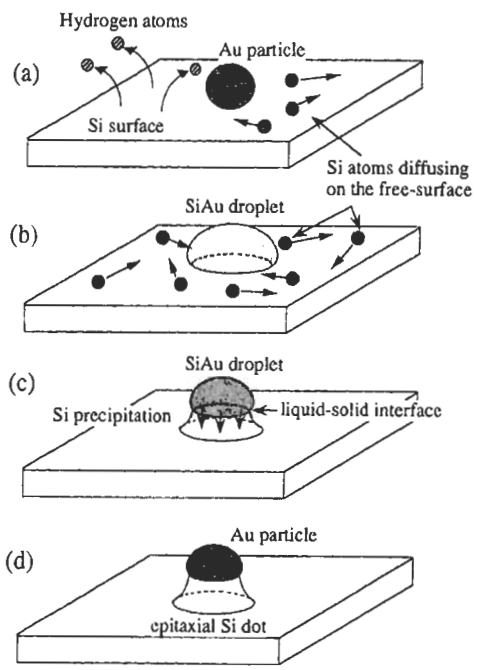


Fig.3 Kinetics of surface droplet epitaxy (SDE). (a) Removal of the hydrogen atoms permits the Si atoms to diffuse over the clean surface at elevated temperature. (b) Surface-diffusing Si atoms are incorporated into the Au particles to form SiAu droplets. (c) Si atoms are precipitated from the alloy droplet during the cooling process. (d) Si and Au were separated at room temperature to form bilayer dot on the flat surface.

The treatments involved in this process are only thermal annealing and cooling in high vacuum and do not require any conventional patterning techniques. In this sense, this process can be regarded as a kind of self-assembly process. Here, good cleanliness of the surface of the Si substrate is quite essential. Actually, even though a direct contact between the Au particle and Si substrate is formed, if the Si surface is partially covered by the oxide layer, thermal annealing results in an interdiffusion of both elements across the original Au/Si interface. Then, the oxide layer suppresses the surface diffusion of the Si atoms and bilayer dot formation [16].

Judging from the above-mentioned discussion, SDE should take place in any eutectic binary system which undergoes an endothermic reaction. Next, we demonstrate a similar experimental result for the Ag-Si system.
Figure 4(a) shows a cross-sectional TEM

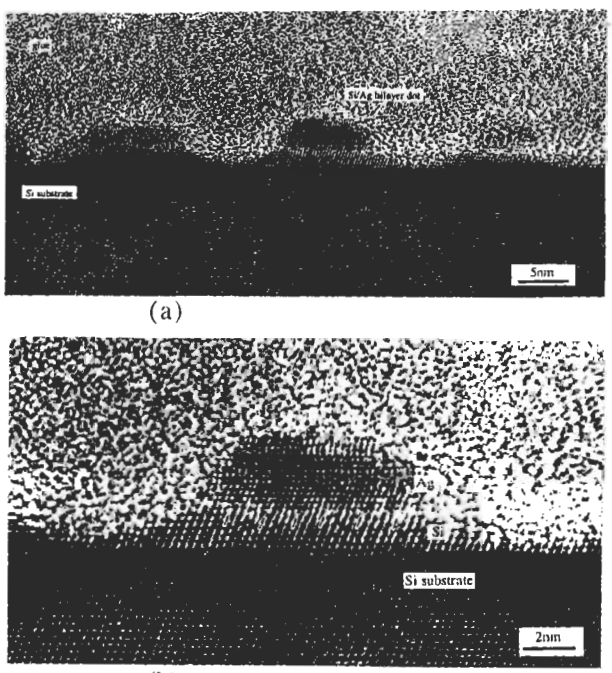


Fig.4 (a) Cross-sectional TEM image of post-annealed specimen. Ag-Si bilayer dots were observed, as shown by arrows. (b) Enlarged TEM image. As indicated by arrows, edge dislocations were present along the Ag-Si interface.

image of a heat-treated specimen, viewed from the [$\bar{1}$10] direction. Ag nanoparticles were produced at the Ar pressure of 4 Torr. The bilayer dots are observed, as shown by arrows in this image. Compared to the Au-Si binary system, higher annealing temperature, 950 ℃, was required in order to fabricate these Ag-Si bilayer dots. This is considered to be due to the higher eutectic temperature, 830℃, and lower solubility of Ag into Si.

An enlarged TEM image is shown in Fig. 4(b). Both the Si dot and Ag particle, which are consistent with the orientation of the Si substrate, are clearly observed in lattice images. Careful observation reveals that edge dislocations are present along the Ag-Si interface, as indicated by arrows. Lattice mismatch between Ag and Si is about 25 %. Therefore, one edge dislocation is necessary for every four lattice planes of Ag along the interface to accommodate the lattice mismatch in order for the epitaxial relation to be obtained [17], [18]. In Fig. 4(b), thirty-five (111) lattice planes are observed in the Ag particle. Thus, eight or nine (111) lattice planes should be present as extra half planes that form the edge dislocation. However, only six dislocations could be observed in this image. In order to compensate the shortage of two or three dislocations, the lattice constant of the Ag(111) is found to become larger than that of the bulk Ag by about 10%. That is, expansion of the lattice constant, in addition to dislocations, is responsible for the accommodation of the lattice mismatch. Such a considerable expansion of the lattice constant could be observed in the relatively small metal particles of less than about 5 nm in diameter in both Ag-Si and Au-Si binary systems [11]. Accordingly, this characteristic structure was considered to be the result of a size effect, i.e., minimization of the total energy of the bilayer dot structure.

4. Conclusion

Metal/Si bilayer dots on a nanometer scale were fabricated on the flat surface of a Si substrate. The kinetics was regarded to correspond to the self-assembly process through liquid phase epitaxy. Then, the surface diffusion of the Si atoms plays an important roll for the bilayer dot formation. Hence, this process was named surface droplet epitaxy (SDE). SDE, which should occur in any eutectic and endothermic system, was observed in the Au-Si and Ag-Si binary systems in this study. Additionally, some characteristic structures, i.e., considerable expansion of the lattice constant and an epitaxial relation between metal and Si, were shown and ascribed to the size effect of these nanometer-sized materials.

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