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Catalytic Effect of Cu Precipitates for the Growth of ZnO Rods

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Pyramid shaped Cu precipitates were formed on Si (100) surface as a result of 200 keV Cu ion implantation at room temperature and subsequent annealing. The Cu precipitates were copper silicide and mainly Cu_4Si. Then ZnO rods were grown on the annealed Cu implanted substrate by chemical vapor transport (CVT). ZnO rods were grown almost perpendicularly to the substrate and their average number density was increased as increasing that of Cu precipitates. These indicate Cu precipitates served as the catalysis for the growth of ZnO rods.

Key words: ion implantation, precipitates, catalysis, Si substrate, ZnO rods

1. INTRODUCTION

One dimensional semiconductive materials such as Si wires [1], GaN tubes [2], ZnO rods [3] have been paid much attention because of its excellent physical properties. In particular, among those attractive materials, ZnO rods have been expected as a promising candidate for the light-emitting device operating at room temperature with a wide band gap (3.36 eV) and the large exciton binding energy (60 meV). For the growth of ZnO rods, the substrate dispersed with catalysis such as Au was often used [4-6]. ZnO rods were selectively grown at the location where the catalysis is dispersed on the substrate.

In case of the epitaxial growth of ZnO rods on the substrate using the catalysis, a few materials including sapphire (α-Al_2O_3) and Si have been used as substrates [3-6]. Although sapphire is the most useful substrate for the epitaxial growth of ZnO rods, it is an insulator and not suitable for processing. For future application of ZnO rods to integrated optelectronic devices fabricated by the conventional Si processing technology, it is very important to develop the technique to control the growth of ZnO rods on Si substrates. However, the lattice parameter and crystal structure of ZnO are quite different from those of Si, it is very difficult to grow ZnO rods on a Si substrate. So far, the growth of ZnO rods on a Si substrate has been attempted, most of ZnO rods were grown inclined to the substrate [6]. To exploit the application of ZnO rods to novel integrated devices, the technique is required to grow ZnO rods perpendicularly to Si substrate.

Implantation of metal ion into a Si substrate has been utilized to produce various metal silicides with specific microstructures on the surface region, such as precipitates and clusters [7,8]. The metal silicide including copper silicide has often formed as a result of ion implantation and annealing process [9], and it is well known that "mixing" structure has appeared in which metal silicide island were surrounded by polycrystalline Si grains [10]. The morphology of the "mixing" structure is similar to that of metal silicide formed inside a hall of a template of polycrystalline Si, therefore, it is expected to serve as the catalyst for the growth of ZnO rods perpendicularly to the substrate.

In this present study, ZnO rods with approximately 1 μm in diameter were successfully grown almost perpendicular to the annealed Cu-implanted Si substrate. The average number density of ZnO rods increased with increasing that of Cu precipitates. Surface morphology of Cu precipitates was observed and its effect on the growth of ZnO rods was investigated.

2. EXPERIMENTAL

Si (100) wafers were cleaved and used as substrates. Typical size of the substrates was 5 mm x 5 mm. The substrates were cleaned by ultrasonic cleaner with acetone and ethanol. Cu ion implantation was made with a 400 kV ion implanter at fluence up to 5×10^{16} atoms/cm^2, an implantation energy of 200 keV and ion current of approximately 3 μA/cm^2 in a vacuum of 10^{-5} Pa. After the Cu ion implantation, the Cu implanted substrates were annealed at 773 K for 1 h under Ar atmosphere using an electric furnace.

Subsequently ZnO rods were grown on the annealed

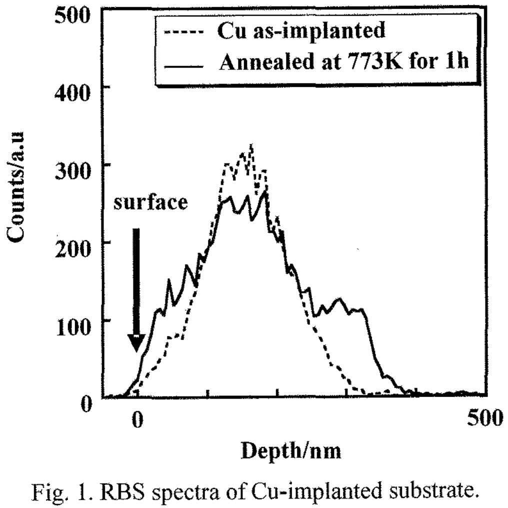

Fig. 1. RBS spectra of Cu-implanted substrate. (a) As-implanted and (b) annealed at 773 K for 1 h. The Cu fluence was 5 x 10 ^{16} atoms / cm^2.

Cu-implanted substrate using the chemical vapor transport (CVT) technique. Ar was used as the carrier gas and the gas flow rate was 80 sccm. Mixed powder of graphite (99.9 %) and ZnO (99.99 %) was put into the alumina boat then was placed at the upstream of the quartz tube. Annealed Cu-implanted substrate was also placed at the downstream of the tube which was heated up to 1223 K for 15 minutes. Surface morphology of the annealed Cu-implanted substrates and ZnO rods were observed using field emission scanning electron microscopy (FE-SEM, JEOL JSM-6700F). Crystal structure of the annealed Cu-implanted substrates and ZnO rods were characterized using X-ray diffraction (Phillips X'Pert-MRD). Rutherford backscattering spectroscopy (RBS)/channeling analysis using a 3 MV single ended accelerator was employed to characterize the Cu-implanted substrate. The analyzed 2.0 MeV $^4He^+$ ions were incident and backscattered particles were detected at 165° scattering angle with a surface barrier detector.

3. RESULTS AND DISCUSSIONS

Figure 1 shows the distribution of Cu atoms in the annealed Cu-implanted substrate. The Cu fluence was 5 x 10^{16} atoms/cm^2. The dashed and solid lines show the distribution of implanted Cu atoms in (a) the Cu as-implanted substrate and (b) the Cu-implanted substrate annealed at 773 K for 1 h, respectively. In Fig. 1, although the distribution of Cu atoms in the Cu as-implanted substrate had almost Gaussian shape, that was broadened and distorted after the annealing. This distorted distribution indicates that solid-phase epitaxial growth (SPEG) of Cu-implanted substrates occurred [7]. The distorted distribution was also observed for a Cu-implanted substrate annealed for 3 h, and this indicates that the annealing time of 1 h was sufficient for SPEG to be finished, and the diffusion of implanted Cu atoms to the surface ended. After the annealing, the Cu concentration at the surface was twice as large as that of Cu as-implanted substrate.

Figure 2 (a) is an XRD pattern of the as-implanted substrate. The pattern consists of several sharp peaks of copper silicide and broad Cu peak. Surface image of the substrate obtained using FE-SEM showed no precipitates were formed on the surface. This means copper silicide formed inside the as-implanted substrate. Fig. 2 (b) is an XRD pattern of the Cu-implanted substrate annealed for 1 h. Strong peaks are indexed with copper silicide such as Cu_3Si and Cu_4Si. Only a little pure copper is identified with the XRD pattern. This indicates the Cu precipitates formed on the annealed Cu-implanted substrate were copper silicide, and most of those were Cu_4Si.

Figure 3 shows the surface morphology of the Cu-implanted substrate after annealing. The Cu fluence was 5 x 10^{16} atoms/cm^2. Light gray colored precipitates with a diameter of approximately 180 nm formed on the surface. When the Cu-implanted substrate was annealed, implanted Cu atoms diffused to the surface of the substrate. Then the nucleation of the Cu atoms occurred and Cu precipitates formed on the surface. According to the energy dispersive X-ray (EDX) analysis, the Cu concentration of the precipitates was higher than that of the surface of the substrate, which indicates that the pyramid-shaped precipitate shown in Fig. 3 was copper silicide.

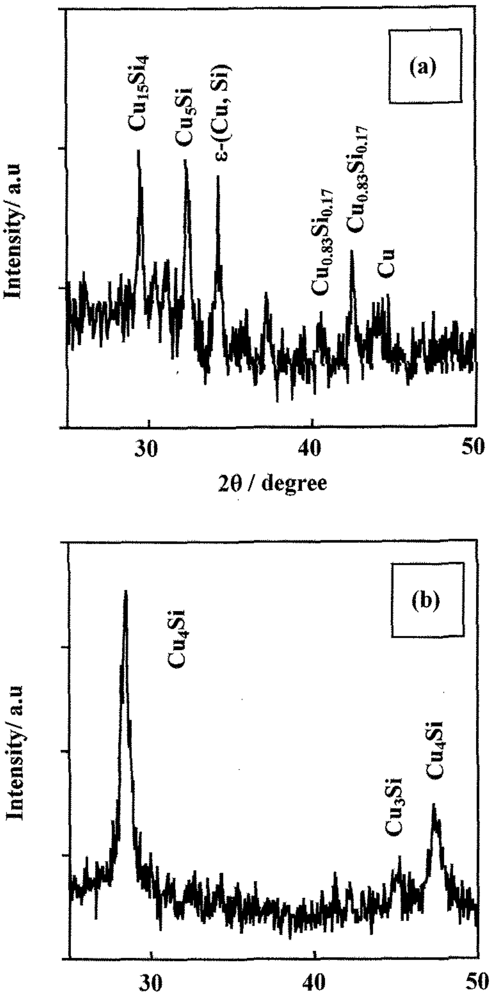

Fig. 2. XRD pattern of the Cu-implanted substrate. (a) As- implanted,(b) Annealed at 773 K for 1 h.

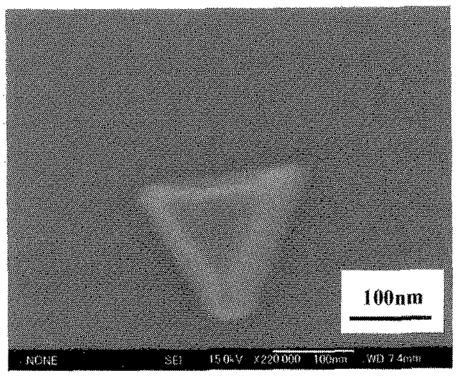

Fig. 3. Surface image of a precipitates after Cu implantation and annealing.

Figure 4 (a) is a surface image of the annealed Cu-implanted substrate after the growth of ZnO rods. The Cu fluence was 5 x 10^{16} atoms/cm^2. Hexagonal shaped rods with a diameter ranging from 400 to 1000 nm and circular shaped rods were also grown on the

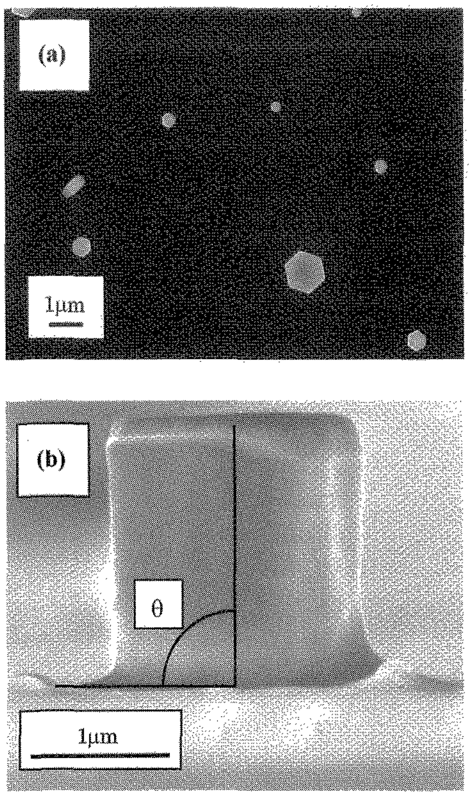

Fig. 4. Surface images of ZnO rods grown on the Cu-implanted substrate.
(a) plane view, (b) cross sectional view.

substrate. Hexagonal shape of the rods indicates the rods had the wurtzite type crystal structure. Therefore, it is thought the rods were single crystalline ZnO rods. This indicates the Cu precipitates served as the catalysis for the growth of ZnO rods. A cross sectional view of the ZnO rod is shown in Fig. 4 (b). A well faceted ZnO rod approximately 1 μm in height was grown almost perpendicular to the surface of the substrate.

Figure 5 shows the distribution of the angle from <0001> direction of ZnO rods to the substrate. More than a half of ZnO rods had the angle of 85-90 degrees. This value is larger than 75-85 degrees as reported before [6]. Considering Si has the diamond type crystal structure and its lattice parameter of a = b = c = 5.43088 Å is quite different from that of a = b = 3.24982 and c = 5.20661 Å of ZnO, it is worth noting that most of ZnO rods which have the wurtzite type crystal structure were grown nearly perpendicular to the substrate.

Figure 6 shows a typical XRD pattern of ZnO rods grown on the Cu-implanted substrate. The pattern consists of (100) and (002) planes of the wurtzite type crystal structure of ZnO. Relatively higher peak of (002) plane shows ZnO rods were preferentially grown on the annealed Cu-implanted substrate along <0001> direction. Although the peak of (100) plane appeared in the pattern, this is derived from some ZnO rods laid on the surface of the substrate as observed in the surface image. Neither Zn nor Cu metal peaks are identified with the XRD pattern. This assures hexagonal shaped rods consisted of pure ZnO.

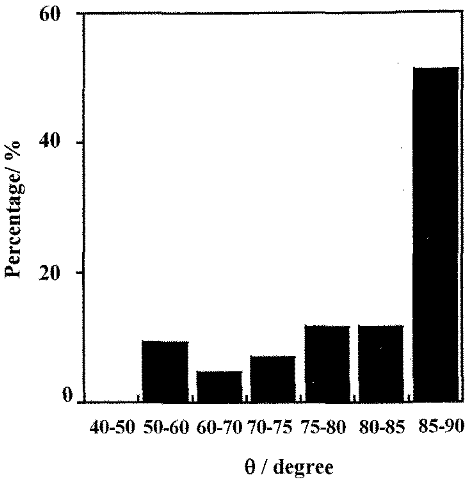

Fig. 5 Distributions of angle from the substrate to ZnO rod.

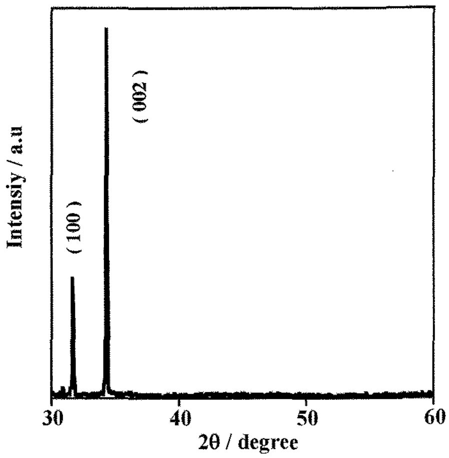

Fig. 6 XRD pattern of the ZnO rods grown on the Cu-implanted substrate.

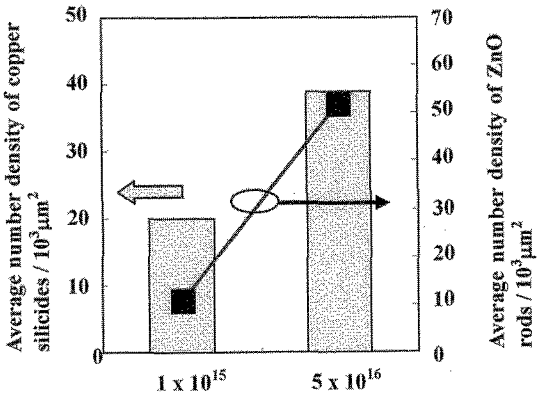

Fig. 7 Relationship of the average density of ZnO rods and copper silicides.

Figure 7 shows a relationship of the average number density of ZnO rods and copper silicides. The measured area for the average number density was 1000 μm². The average number density of copper silicides is increased with increasing the Cu fluence. It is also shown that the average number density of ZnO rods increases with increasing that of copper silicides. Though the average number density of copper silicides is little different from that of ZnO rods at the Cu fluence of 1 x 10^{15} atoms/cm^2, both are the same at the Cu fluience of 5 x 10^{16} atoms/cm^2. This is an evidence that copper silicides were served as the catalysis for the growth of ZnO rods. ZnO rods were selectively grown on the location of Cu precipitates, and the average number density of ZnO rods depends on that of copper silicides.

4. SUMMARY

ZnO rods were successfully grown almost perpendicular to the Cu-implanted substrate. The average number density of ZnO rods increases with increasing Cu precipitates. This fact indicates the Cu precipitates served as the catalysis for the growth of ZnO rods. Ion implantation and subsequent annealing is effective to disperse the catalysis on the substrate for the growth of perpendicularly aligned ZnO rods.

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