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Nanoparticle-Induced Crystallization of Amorphous Ge Film Using Ferritin

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1. Introduction

Polycrystalline germanium (poly-Ge) thin films have attracted a growing interest in recent years because of their higher carrier mobility than poly-Si thin films. Several investigations have been conducted to obtain poly-Ge films by metal-induced lateral crystallization (MILC) [1,2,3], laser annealing and solid-phase crystallization (SPC) [4]. MILC is potentially a promising approach to growing crystalline Ge films at low temperatures. Therefore, the MILC method has been developed using the catalytic effects of Ni [1,2,3]. In this crystallization method, metals migrate toward the amorphous germanium (a-Ge) region, leaving the crystalline Ge phase behind. However, the grains contain small amounts of metal contamination that can deteriorate the device performance [6]. It is therefore necessary to reduce the level of metal contamination for device applications. To reduce the level of metal contamination in a crystallized film, the area of the metal pattern on the Ge film must be minimized. Thus, we have investigated nanoparticle-induced crystallization (nanoparticle MILC) [7]. Nano particles were synthesized using ferritin through a biological method named the bio-nano process (BNP) [8]. In this letter, we report the crystallization of a-Ge using Ni nanoparticles synthesized using ferritin.

2. Experimental

A-Ge films with a thickness of 30 nm were formed on SiO_2 (100 nm)/Si substrates by molecular beam epitaxy using a Knudsen cell while keeping the substrates at room temperature. As the homogeneity of the size of nanoparticles plays an important role in the formation of nucleus sites, we fabricated Ni nanoparticles in the cavity of the cage-shaped ferritin. Ferritin has a spherical cage structure with inner and outer diameters of 7 nm and 12 nm, respectively [9]. Ferritin can crystallize various inorganic nanoparticles inside its vacant cavity by biomineralization [10]. A Ni-oxide core was synthesized in the ferritin. The diameter of the Ni-oxide core in ferritin is around 6 nm. Therefore, approximately 2000 Ni atoms are stored in a single ferritin.

Crystal growth was performed as follows. First, ferritin with a Ni-oxide core was prepared by dilution with pure water. The details have been described in the previous work [7]. Then, ferritin in pure water was dropped onto the a-Ge layer and kept for 10 min. The density of the adopted Ni nanoparticles on the a-Ge surface was estimated from both the SEM image and Ni atom density of the crystallized film. After the adsorption of ferritin, UV/ozone treatment was carried out at 115 ^{o}C for 50 min in order to remove the protein shell. Finally, the samples were annealed at 400 ^{o}C for 10 h in N_2 ambient. To determine the relationship between the Ni impurity in the Ge film and the density of Ni nanoparticles on the Ge film, the ferritin concentrations of 0.5 mg/ml~10^{-5} mg/ml were used. In addition, a conventional MILC process (Ni-pattern MILC) using the Ni thin film with a thickness of 5 nm patterned by electron-beam evaporation on an a-Ge film was also carried out to confirm the role of Ni nanoparticles. The crystal qualities of the grown layers were characterized by Raman spectroscopy, cross-sectional TEM. Film impurity content was measured by secondary ion mass spectrometry (SIMS).

3. Results

Figure 1 shows scanning electron microscopy (SEM) images of Ni nanoparticles on an a-Ge film after UV/ozone treatment with the ferritin concentrations of (a) 0.44 mg/ml, (b) 0.15 mg/ml and (c) 0.088 mg/ml. For reference, the SEM image of the a-Ge surface without nanoparticles is also shown in Fig. 1 (d). The adsorption densities of Ni nanoparticles in samples (a), (b) and (c) were 1.6×10^{11}, 7.6×10^{10} and 3.5×10^{10} dots/cm^2, respectively. The density of Ni nanoparticles adsorbed on to the a-Ge film decreased with decreasing ferritin concentration. Thus, the density of nanoparticles can be controlled by adjusting the concentration of ferritin solution.

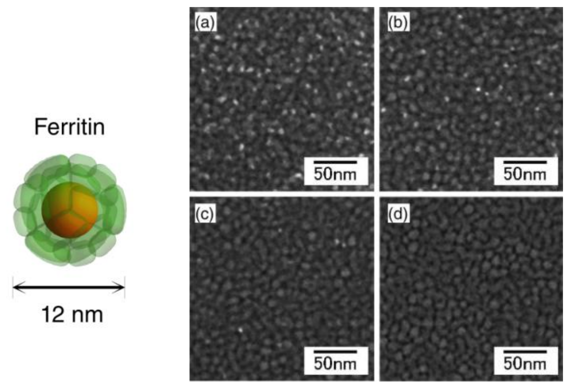

Fig. 1 Schematic of a ferritin protein with Ni core. SEM images of a-Ge surfaces with different nanoparticle densities. (a) 0.44 mg/ml, (b) 0.15 mg/ml, (c) 0.088 mg/ml and (d) without Ni nanoparticles. The white dots show the Ni nanoparticles.

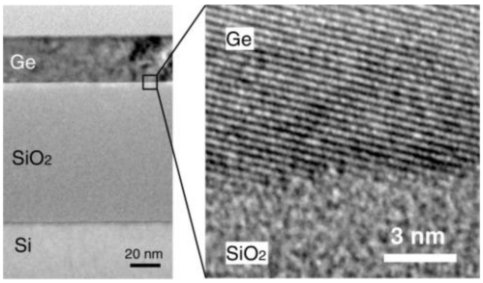

Fig. 2 Cross-sectional TEM image of Ge/SiO_2 interface region of sample after crystallization.

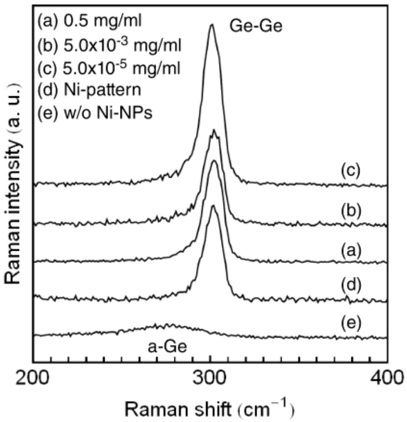

Fig. 3 Raman spectra obtained from different ferritin concentrations (a-b), without Ni nano particles (NPs) (d) and with Ni pattern MILC (e).

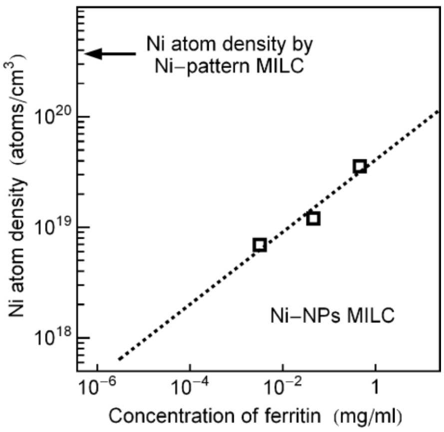

Fig. 4 Relationship between concentration of ferritin solution and Ni atom density of Ni-nanoparticle MILC films. The Ni atom density of Ni-pattern MILC film was indicated by the arrow.

We confirmed crystal growth from the surface down to the interface with the SiO_2 layer by cross-sectional TEM, as shown in Fig. 2. To evaluate the crystal quality in crystallized regions, the Raman spectra were measured in the samples with ferritin concentrations of (a) 0.5 mg/ml, (b) 5.0×10^{-3} mg/ml and (c) 5.0×10^{-5} mg/ml. The obtained results are summarized in Fig. 3. Sharp peaks at about 300 cm^{-1}, which originate from the Ge-Ge bonds, were clearly observed in the samples with Ni nanoparticle and Ni-pattern MILC films. On the other hand, a broad peak at 270 cm^{-1} was observed in the sample without nanoparticles. The broad peak originates from a-Ge. From these results, the Ni nanoparticle MILC method could provide an approximately equivalent crystalline quality with the Ni-pattern MILC method.

SIMS study of the poly-Ge films was carried out. Ni signals from the SIMS depth profiles indicated that Ni atoms were uniformly distributed in 30 nm film. Figure 4 shows the average Ni atom density of the poly-Ge film of nanoparticle MILC using (a) 0.46 mg/ml, (b) 0.046 mg/ml and (c) 3.2×10^{-3} mg/ml ferritin solutions. The Ni atom density decreased linearly in proportion to the decrease of ferritin concentration as shown by the broken line. The average Ni atom density of the Ni-pattern MILC was also shown by the arrow in Fig. 4. The Ni atom density which was carefully measured outside the Ni-pattern was one order of magnitude higher than that of the nanoparticle MILC film. The uniform ferritin adsorption and the optimization of the annealing process would make further reduction in Ni atom density possible.

3. Conclusions

A poly-Ge film was obtained using ferritin with a Ni core and an annealing temperature of 400 ^oC. Owing to the nanoparticle MILC process, the Ni contamination in the poly-Ge film was reduced by more than one order of magnitude compared with that in the case of a Ni-pattern MILC method. Therefore, nanoparticle-induced crystallization provides a more efficient approach to reducing the level of metal contamination.

Acknowledgements

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