Crystallization of amorphous Si by pulse annealing with Ni ferritins

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Keywords: MILC, cage-shape protein, bio-nano-crystallization

Abstract

We investigated an application of supramolecular protein, and demonstrated the metal induced lateral crystallization utilizing ferritins with Ni nanoparticles, named the "bio-nano-crystallization". So far, this method has required long time, because of this method condition based on the conventional solid phase crystallization. In this study, we applied the pulsed rapid thermal annealing to bio-nano-crystallization. As a result, we succeeded in the crystallization for a short time. We found that the TFTs characteristics were improved with decrease metal impieties in poly-Si thin films by this method.

1. Introduction

Recently, poly-Si TFT are widely used as a drive circuit for TFT display. The device performance depends on the quality of the poly-Si thin film thus improvement of grain size and quality of poly-Si is necessary. The metal induced lateral crystallization (MILC) is one of the crystallization methods utilizing metal catalysts for poly-Si fabrication, where lateral crystallization of amorphous Si is carried out after crystalline nucleus formation by annealing of catalyst. As a novel MILC method, we have proposed and been demonstrating a utilization of metal nanoparticle accommodated cage-shaped supramolecular protein as device fabrication nanocomposite. Here we use a ferritin for electric device by choosing a biochemically synthesized inorganic nanoparticles formed in the vacant cavity of it[1]. Figure 1a depicts a schematic cross-sectional drawing of ferritin structure with an accommodated inorganic nanoparticle. In nature, the ferritin accommodates iron oxide nanoparticle in the cavity. In addition it is reported that the ferritin can form different kinds of metal and semiconductor nanoparticles in the vacant cavity by biomineralization[2] such as Nickel oxide. Our novel MILC method utilizing this Ni oxide accommodated ferritin (Ni-Ferritin), and we call this method as "bio-nano-crystallization" (BNC)[3]. We demonstrated a fabrication of poly-Si thin film with a combination of BNC and the condition of conventional solid phase crystallization (SPC)., and resulting poly-Si film showed large grain size. However the conventional SPC required long time. In this study, we combine the BNC and the pulsed rapid thermal annealing(PRTA) [4] to realize quick poly-Si crystallization and to improve the film quality. We also introduce microscopic method for the evaluation of fabricated poly-Si film which is made by BNC-PRTA.

2. Experimental

Ni-ferritins were adsorbed on 50nm-thick amorphous Si (a-Si) thin films. Successive UV/O_3 treatment was used for the removal of an outer protein shell of ferritin and the formation of Ni silicide which work as a nucleus for the lateral Si crystallization. For a crystallizstion of a-Si, Ni-ferritin adsorbed a-Si substrates were annealed at maximum temperature of 740^{o}C (pulse width; 13sec) by PRTA. After the crystallization by PRTA, we have observed the samples by optical microscopy and done the crystalline mapping by Raman microscopy. We also fabricate the top gate type n-channel TFTs using crystallized poly-Si thin films and measured the electric properties of them.

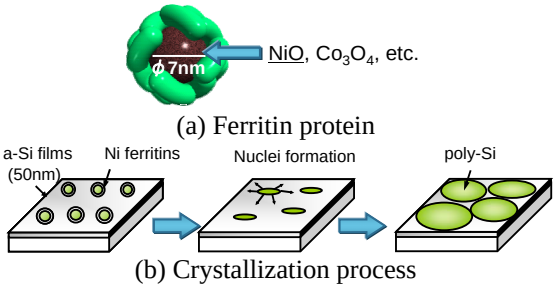

Fig.1. Schematic drawing of the bio-nano-crystallization

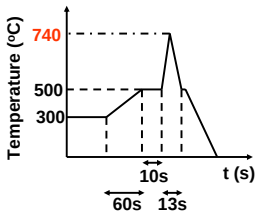

Fig.2. Temperature profile of RTA

3. Results and discussion

Raman mapping

Ni-nanoparticle accommodated ferritin (protein concentration: 0.3mg/ml) were adsorbed on a-Si thin films and form the monolayer of Ni-ferritin of the substrate. After the UV-Ozone treatment, the sample substrate was annealed by PRTA to form poly-Si. Fabricated poly-Si substrate was observed by the laser Raman spectroscope (nano photon product, RAMAN-11) with the exciting wavelength at 532nm for the evaluation of crystallinity of fabricated poly-Si. We applied different numbers of temperature pulse to elucidate the effect of the pulse number. An optical microscope image of the poly-Si annealed with a single pulse is shown in Fig. 3a. As we can see in the image, crystallized a-Si appears circular in the image. The poly-Si crystallized parts were appeared darker than the surrounding a-Si part. An averaged area size of poly-Si is approximately 8.4μm in diameter.

A point resolved Raman spectroscopy has done at the same area of the sample as well as depicted in Fig. 3a. Figure 3b depicts a peak intensity mapping of obtained Raman spectra. As shown in Fig. 3c, the crystalline Si and amorphous Si show the peak are 520cm^{-1} and 470cm^{-1}, respectively. The color indicated the red and green in Fig. 3b correspond to 520cm^{-1} and 470cm^{-1}, respectively. The crystallized areas showed the peak at 520cm^{-1} and could be distinguished according to the intensity distribution of Raman spectra.

In contrast to single pulse annealed sample, the sample annealed with the 3-pulse PRTA showed the crystallization in whole observed area. As a result, we observed the Raman peak of 520cm^{-1} was detected from whole surface; it indicates that the whole sample area was crystallized completely.

The initial thin film is an amorphous structure that has much more gap than crystalline structure due to irregular crystal alignment. If the same atomicity as amorphous-Si, it is considered that the crystallized Si domain becomes a little smaller than that of amorphous Si, and the little tensile stress worked at the grain boundaries. The rearrangement of silicon atoms at the grain boundary after the crystallization is schematically drawn in Fig.4. It is reported that the position of crystalline phonon peak of stress containing crystal will be negatively shifted by tensile stress [5]. Therefore the mapping of crystal phonon peak shifts from 520cm^{-1} can be used as an indication of the position of grain boundary. The result was shown in Fig.5. As we expected, the domain boundary of crystallized domain showed the negative shift of the Raman peak. The averaged crystal grain size is estimated to be 14.8μm from a negatively peak shift position.

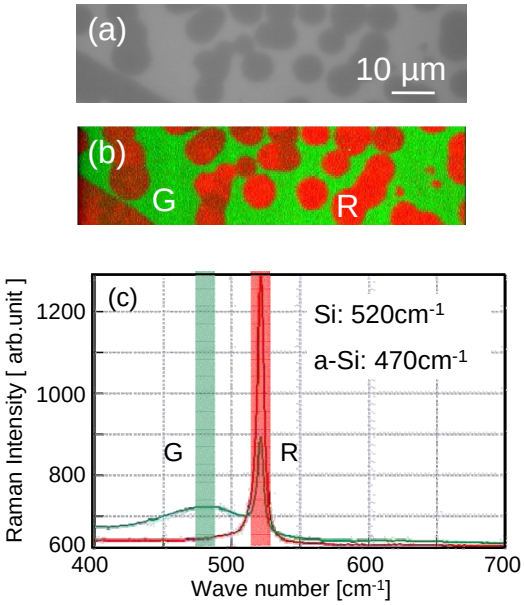

Fig.3. The Raman spectroscopy results of the sample annealed with single pulse. (a) an optical image, (b) Raman mapping, and (c) Raman spectra at crystalline (R) and amorphous (G) part.

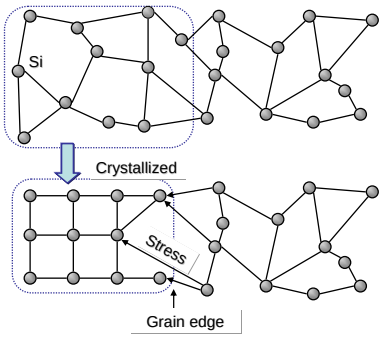

Fig.4. A schematic drawing of induced stress during the crystallization at the grain boundary.

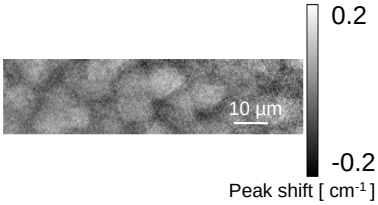

Fig.5. Peak shift mapping image of a 3-pulse PRTA crystallized Si surface. Peak shift in the image is difference from 520cm^{-1}.

The effect of Ni ferritins concentration

We also studied the effect of Ni catalyst amount by using different concentration solution of Ni-ferritin. We applied 0.045 or 0.450 mg/ml Ni-ferritin solution for the formation of Ni silicide nuclei. Here we applied a 3-puls-PRTA. The optical microscope images of each sample and the distribution of grain size are summarized in Fig.6 and Fig.7, respectively. In the case of 0.045 mg/ml, the thin film was not wholly crystallized. As we can see in Fig. 6a, Crystallized domain shows large distribution of grain size from a few to ~ 60 μm^2 (Fig. 7a). The mean grain size is small (18.0 μm^2), however, the maximum grain size can be very big (106.0 μm^2). When we use the low concentration solution, the aerial density of adsorbed Ni-ferritin, i.e. Ni silicide nuclei in unit area, is small. Because the intervals of crystalline nucleus were wide, the crystalline grains could grow without collision to other grains. Therefore, some individual grain can grow very large.

Meanwhile, in a case of higher concentration (0.45 mg/ml), we observed whole crystallization on observed area. It suggests that 0.45 mg/ml Ni-ferritin solution is enough to induce whole crystallization. We observed three peaks in the grain size distribution (Fig. 7b); at 15, 30 and 60 μm^2. The average grain size was 21.5μm^2. In case of condensed solution, the crystalline nucleus density was high. It was thought that the crystallization was obstructed by the collision of the some crystal grains, thus the average crystallized domain become smaller. The comparisons of different concentration solutions suggest that the whole area crystallization and large domain formation can be controlled by adjusting catalyst Ni concentration. The exploration of the most suitable crystallization condition is under investigation.

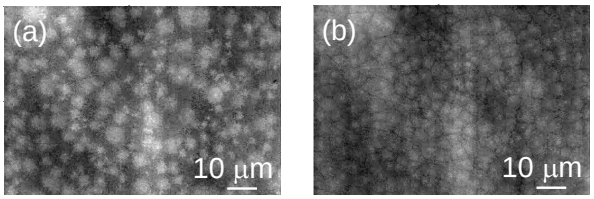

Fig.6. Ni-ferritin concentration dependence on crystallization. Optical microscopy images of poly-Si crystallized with (a) 0.045 mg/ml, and (b) 0.45 mg/ml Ni ferritin solution.

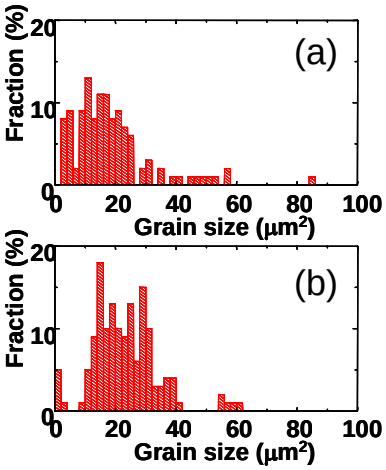

Fig.7. Grain size distribution of crystallizaed by(a) 0.045 mg/ml, (b) 0.45 mg/ml of Ni-ferritin.

TFT characteristics

We prepared TFTs by conventional SPC (without Ni ferritins) and BNC (with Ni ferritins) for evaluating the electronic characteristics of these devices. Transition characteristics of fabricated TFTs are shown in Figs. 8. Channel width and length are W/L=10/5 μm, respectively. BNC method used Ni as metal catalyst, but the characteristic of TFT made by BNC have the low off leakage current equivalent to that of TFT made by conventional SPC. This result indicated that the metallic impurities were suppressed to extremely low level to 1×10^{18} atoms/cm^3 by BNC. In addition, on/off ratio and subthreshold characteristics was improved with decrease the off leakage current. Meanwhile, the field effect mobility was extremely improved to 20.9cm^2/Vs, because of improvement of the quality poly-Si by increase of grain size.

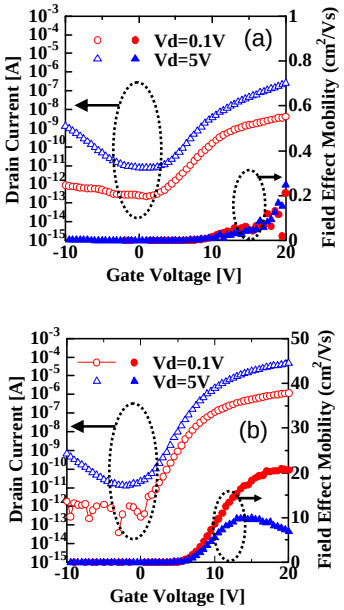

Fig.8. Transmission characteristics of poly-Si TFTs fabricated with (a) conventional SPC (w/o Ni ferritins) and (b) BNC (with Ni ferritins).

4. Summary

We proposed a-Si crystallization utilizing a combination of the Ni-nanoparticle-accommodated ferritins and the short time crystallization by applying the PRTA. As a result of Raman mapping, it was confirmed that the growth area from crystalline nucleus of Ni-ferritins was the crystallized areas, and extremely large size crystalline grain was observed. Furthermore, in the TFT characteristics, the off leakage current was able to be suppressed to conventional SPC by decrease the metallic impurities, the electrical properties were improved. Therefore, BNC is promising for preparation of high efficiency TFTs.

Acknowledgement

We thank to Dr. Taisuke Ohta in nano photon for the Raman mapping in this study. This study is supported by the Core Research for Evolutional Science and Technology, Japan Science and Technology Agency.

5. References

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