

# Positional control of crystal grains in silicon thin film utilizing cage shaped protein

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## 1. Introduction

Recently, polycrystalline silicon (poly-Si) thin film transistors are expected as driving circuit for various next generation displays. The device performance depends on the quality of the poly-Si thin film, thus improvement of grain size and quality of poly-Si is important. The metal induced lateral crystallization (MILC) [1] is one of the crystallization methods utilizing metal catalyst, where lateral crystallization of amorphous silicon proceeds from crystalline nuclei by the help of catalyst. We have proposed and demonstrated several kinds of silicon device by utilizing cage-shaped supramolecular protein, called ferritin [Fig.1]. The ferritin can form various kinds of inorganic nanoparticle such oxide materials as iron oxide or nickel oxide [2] in vacant cavity by biomineralization. Previously we proposed a crystallization method utilizing Ni ferritins as metal catalysts named "bio-nano-crystallization (BNC)". We demonstrated a fabrication of poly-Si thin films by BNC at 550°C for 24 hours, and several tens micrometer size poly-Si was obtained [2]. However, the positions of grain boundaries were randomly located.

In this study, we modified the BNC by employing the selective adsorption of ferritins to realize the location control of grain boundaries in silicon thin film.

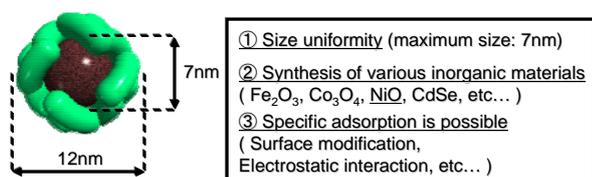


Fig.1 Schematic and features of ferritin

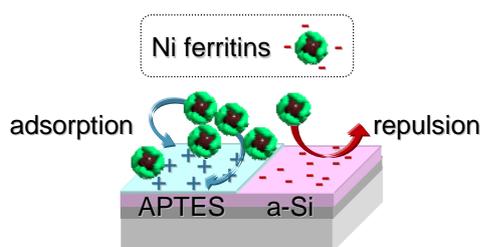


Fig.2. The selective adsorption of ferritins by APTES

## 2. Experimental details

### Preparation process

50 nm-thick amorphous silicon (a-Si) were deposited by LPCVD, and Ni oxide accommodated ferritins were adsorbed on a-Si thin films. Successive ultraviolet ozone irradiation was performed for the elimination of outer protein shells and the formation of nickel silicide as nucleus. For crystallization, a-Si thin films with adsorbed Ni nanoparticles were annealed at 550°C for 24 hours. The selective adsorption was performed by utilizing 3-amino-propyl-triethoxysilane (APTES;  $\text{H}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_2\text{CH}_3)_3$ ) as the electrostatic adsorption patterns [3]. Ferritins were adsorbed for 1 min after patterning of APTES.

## 3. Results and discussion

### Controls of adsorption densities

We tried the location control of ferritins adsorption. In previous work, it was confirmed that ferritin surface and  $\text{SiO}_2$  have negative charge, and APTES have positive charge as shown in Fig.2. So, ferritins were attracted to APTES areas. We investigated the effect of ferritin concentration, and the adsorption densities measured by scanning electron microscope are summarized as shown in Fig.3. When APTES was not formed on  $\text{SiO}_2$ , adsorption densities were saturated within 3 minutes for ferritin with a concentration of 0.5 mg/ml and 0.25 mg/ml. The amount of ferritin of 0.05mg/ml and 0.025 mg/ml are too low, so adsorption densities could not be measured precisely. Meanwhile, highest adsorption density was observed on the substrate with APTES, and there were little dependency on the treatment time. Therefore, it was concluded that the adsorption selectivity was highest when the adsorption time is 1 minute.

According to the strategy mentioned above, we tried location control of adsorption areas utilizing APTES patterns, and 0.5 mg/ml Ni ferritin adsorbed on substrate was shown in Fig.4. The adsorption densities with and without APTES are  $2.5 \times 10^9 \text{ cm}^{-2}$  and  $1.1 \times 10^{11} \text{ cm}^{-2}$ , respectively. These densities were almost similar densities expected in the previous experiment shown in Fig.3, thus, the selective adsorption of ferritins was achieved utilizing APTES patterns on the same substrate.

### Positional control of crystal grains

Next, we tried the location control of crystal grains. According to previous work, in the case of 0.5mg/ml Ni ferritin, crystalline nuclei were formed with the mean interval of approximately 6.8  $\mu\text{m}$ . Therefore, when the APTES pattern size is smaller than the mean interval of crystalline nuclei, it is expected that the single crystal grain can be obtained on the single APTES pattern. Therefore, the APTES pattern was designed 5  $\mu\text{m}$  square. And the interval of patterns was 10  $\mu\text{m}$  then Ni ferritins (0.5 mg/ml, pH 8.0) were adsorbed on patterned a-Si substrate. After ferritins adsorption, samples were annealed at 550°C for 24 hours. The grain boundary was observed by SEM after secco etching as shown in Fig. 5. We could confirm that crystal grains were selectively formed on APTES patterns and large square grain boundaries of approximately 10  $\mu\text{m}$  were formed. However, these grains had many internal grain boundaries. And extra crystal grains were observed even at diagonal position. As for the causes of diagonally located, it was thought that the distances of patterns at diagonal position was approximately 14  $\mu\text{m}$  and that the area of weak electrostatic interaction between ferritins and APTES was formed, accordingly Ni ferritins were absorbed there. Hence further optimization of the process is required.

### 3. Conclusions

We proposed a novel MILC process utilizing Ni oxide accommodated ferritins and their electrostatic interaction with APTES patterns. As a result, the adsorption densities and adsorbed position were controlled by ferritin concentration. We tried the location control of crystal grains by patterning APTES. Crystal growth corresponding to the APTES patterns was confirmed. We succeeded in obtaining position-controlled large silicon grains.

### Acknowledgements

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### References

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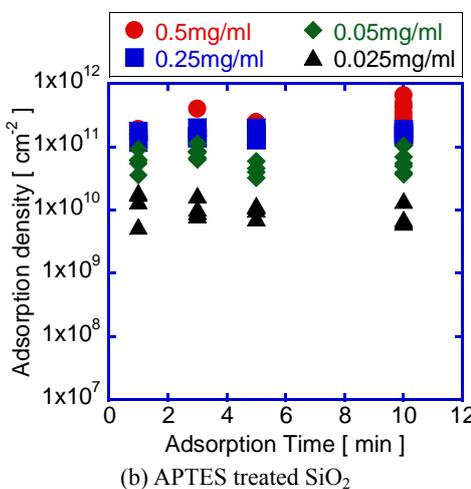
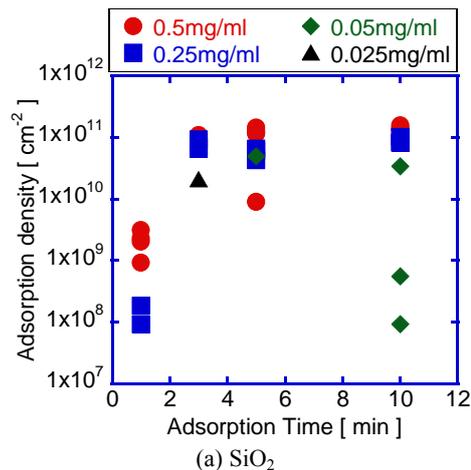


Fig. 3. Concentration and APTES dependency of adsorption densities

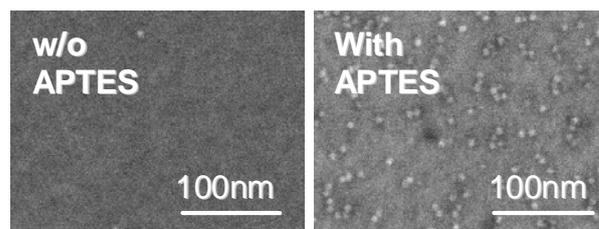


Fig.4. Adsorption state of ferritin on APTES patterned substrate (0.5mg/ml)

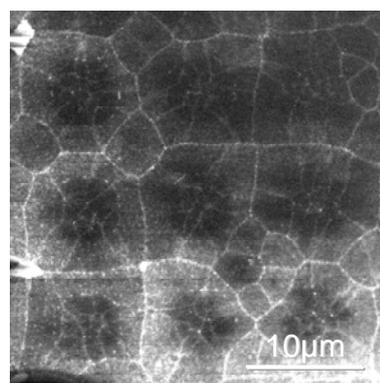


Fig.5. Poly-Si film crystallized by combining BNC with APTES patterning