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Growth of Si Nanowire Using Metal-Induced Lateral Crystallization

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1 Introduction

Metal induced crystallization, where metal such as Ni acts as a "catalyst", offers low temperature crystallization of amorphous Si (a–Si). This phenomenon has been applied to positioning of single–crystal Si grains using a nano–imprint technology [1, 2] and to the formation of polycrystalline Si films on glass substrates using metal–induced lateral crystallization (MILC) [3] phenomenon. Most of the study carried out to date has been aimed at preparing Si films for thin–film transistor application.

In MILC, our previous study has found from in–situ transmission–electron microscopy that the MILC process using Ni is initiated by needle–like crystallites which moves along one of ⟨111⟩ crystal directions. [4] In the conventional MILC process, however, the needle–like crystallite does not grow for long distance but it frequently changes its direction to another equivalent ⟨111⟩ direction. Therfore it appears that, in macroscopic view, the crystallization front is almost uniform.

Our new finding, which we report in this paper, is that the needle–like crystallite growth continues for long distance without changing its direction when supply of Ni is reduced and the crystallization temperature is reduced. As the result, we can grow single–crystal Si wires having about 100nm in width and up to 20μm in length. This phenomenon will be of great interest to develop a new fabrication method of single–crystal Si nanowires. This paper also reveals that Ni diffused into a–Si prior to the growth of needle–like crystallites strongly affects the growth characteristic.

2 Limited–Supply Ni MILC

In the case of conventional–MILC (Fig. 1(a)) where Ni film directly deposited on the a–Si film, a large amount of Ni is introduced into the a–Si, which results in lateral crystallization with macroscopically uniform growth front. On the contrary, when a layer is introduced between the a–Si film and the Ni layer to reduce the supply of Ni (Fig. 1(b)), crystallization phenomenon changes and growth of long Si nanowires takes place.

In the experiment, Ni supply to a–Si was reduced by incorporating a thin chemically grown SiO_2 layer between the a–Si film and the vacuum evaporated Ni film. The a–Si was deposited on oxidized Si wafer using UHV-evaporation. The thickness of a–Si films was changed from 50 ~ 300nm to investigate growth characteristic. The cap SiO_2 layer was formed by the Spin–on–Glass (SOG)–SiO_2. After opening the Ni supply windows in the cap SiO_2 layer, the supply–limiting layer was formed by the treatment in a boiled of mixture of NH_4OH:H_2O_2:H_2O(1:1:2) for 15min. Ni was deposited by vacuum evaporation and its thickness was 10nm. The sample was first annealed at 600°C for 10min to initiate the conventional MILC, in other words, lateral crystallization with uniform growth front. At this stage, unreacted Ni was removed with HCl:H_2O_2(1:1) solution. The sample was then annealed at 550°C in an N_2 ambient to grow Si nanowires.

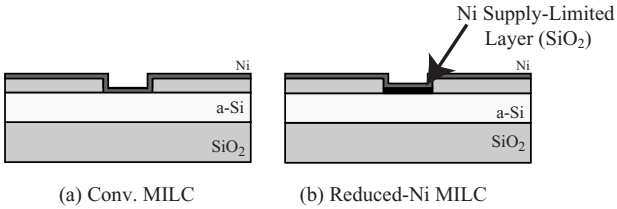

Fig. 1 Schematic cross-section of samples prepared for (a) conventional-MILC and (b) limited Ni supply MILC.

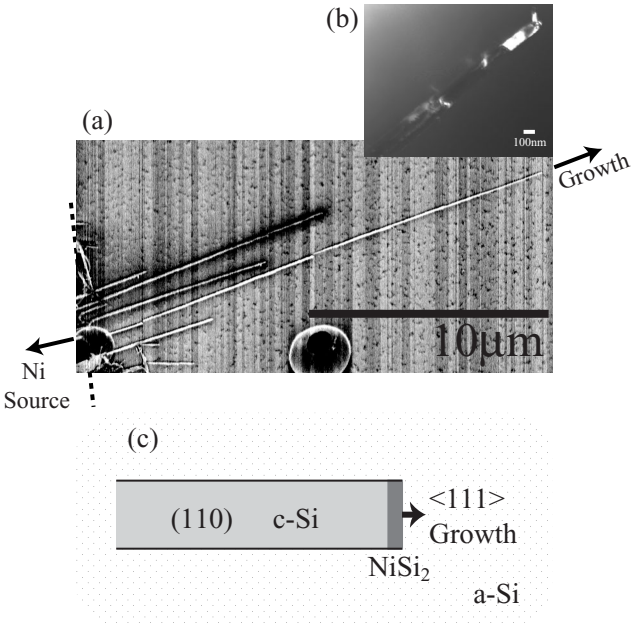

Fig. 2 (a) SEM image of Si-nanowires after annealing at 550°C for 20 hours. The a-Si thickness was 100nm. (b) TEM plain–view image of a nanowire. (c) Schematic top–view of nanowire growth. The nanowire has ⟨110⟩ along the surface normal direction and the growth proceeds along ⟨111⟩ direction.

3 Growth Characteristics of Si Nanowire

Fig. 2(a) shows scanning electron microscope (SEM) image of Si nanowires formed from an a–Si film having 100nm thickness. The sample was annealed at 550°C for 20 hours. Prior to observation, Si wires were chemically delineated. We can clearly see that crystalline Si wires having about 100nm in width and up to 20μm in length grow.

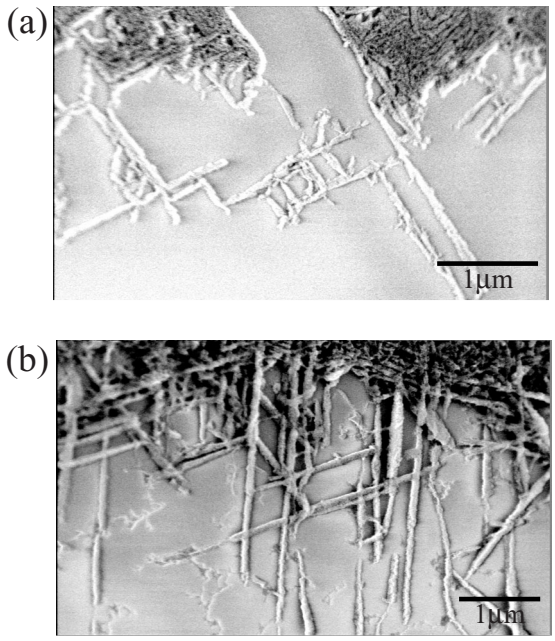

Fig. 3 SEM image of a Si-nanowires after annealing at 550°C for 20 hours. The a-Si thickness was (a) 50nm and (b) 200nm.

In Fig. 2(b), transmission electron microscope (TEM) plain–view taken from a Si wire is shown. It has been fount from TEM that the wires are single crystal Si having a small slice of $NiSi_2$ at the growth front of the wire. Diffraction patterns showed that, as is illustrated in Fig. 2(c), the Si wire has ⟨110⟩ along the surface normal direction and the growth proceeds along ⟨111⟩ direction where $NiSi_2$ has the minimum surface free energy.

The growth characteristic of the Si nanowires has been found to depend on the thickness of the a–Si film. When the a–Si film was thin (Fig. 3(a)), the wires were observed to frequently changes the growth direction and the blanching of the wire during growth frequently took place. It is noteworthy that, in the case that the a–Si film is thin, the width of the wire broadens as the growth proceeds and the width shrinks when the growth direction changes or the blanching takes place.

When the thickness of a–Si film increased to 200nm (Fig. 3(b)), similarly to the result shown in Fig. 2(a), the Si nanowires grow straight. However, as can be seen in Fig. 3(b), the Si nanowires overlap each other. This suggests that, when a–Si film is thick, a–Si remains over or under the nanowires.

Figure 4 shows the change in width of the single–crystal Si nanowires with growth distance. Two wires were sampled for each a–Si thickness. The results suggest that, for 50nm–thick a–Si, the width changes periodically. This implies that the change in growth direction and blanching observed for 50nm–thick a–Si take place after growing for a certain distance.

4 Discussion

In addition to the results shown above, we have observed the following two phenomena. (1) When the annealing lasted long, spontaneous nucleation becomes to take place in a–Si. Th density of the spontaneous nuclei is clearly Gaussian distributed along the distance from the MILC growth front. (2) Under the limited Ni supply condition. crystallization is strongly dependent on the pattern of the Ni source. These facts indicate that Ni diffuses into a–Si faster than the crystal growth and the growth characteristic is strongly dependent on the amount of Ni in a–Si. From this point of view, the a–Si thickness dependent growth characteristic of the nanowires could be accounted for as follows. If we assume that the amount of Ni supplied to a–Si is constant, Ni concentration becomes high as the a—Si film thickness becomes thin. In the ideal case, when a $NiSi_2$ crystallite moves, the rate of Ni incorporation from the a–Si and the rate of Ni remained in crystal Si balanced. But, in the case where Ni concentration is high, the rate of Ni incorporation becomes large enough to increase the size of $NiSi_2$ crystallite and blanching and changing direction frequently take place.

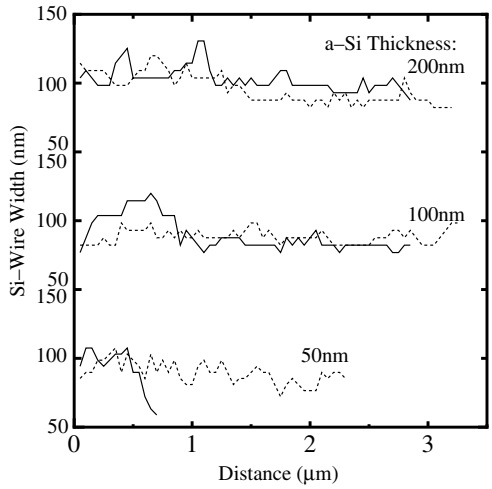

Fig. 4 Change of Si nanowire width with growth length. Two wires sampled for each a–Si thickness.

5 Conclusions

We have fount that, by reducing the supply of Ni in the MILC process, single crystal Si nanowires can be grown. The width of the wires is about 100nm. The growth length up to 20μm was observed. The experimental results suggest that the amount of Ni diffused into a–Si is a key factor to grow such long nanowires.

Acknowledgments

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