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Nickel-disilicide-assisted excimer laser crystallization of amorphous silicon*

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Polycrystalline silicon (poly-Si) thin film has been prepared by means of nickel-disilicide ($NiSi_2$) assisted excimer laser crystallization (ELC). The process to prepare a sample includes two steps. One step consists of the formation of $NiSi_2$ precipitates by heat-treating the dehydrogenated amorphous silicon (a-Si) coated with a thin layer of Ni. And the other step consists of the formation of poly-Si grains by means of ELC. According to the test results of scanning electron microscopy (SEM), another grain growth model named two-interface grain growth has been proposed to contrast with the conventional Ni-metal-induced lateral crystallization (Ni-MILC) model and the ELC model. That is, an additional grain growth interface other than that in conventional ELC is formed, which consists of $NiSi_2$ precipitates and a-Si. The processes for grain growth according to various excimer laser energy densities delivered to the a-Si film have been discussed. It is discovered that grains with needle shape and most of a uniform orientation are formed which grow up with $NiSi_2$ precipitates as seeds. The reason for the formation of such grains which are different from that of Ni-MILC without migration of Ni atoms is not clear. Our model and analysis point out a method to prepare grains with needle shape and mostly of a uniform orientation. If such grains are utilized to make thin-film transistor, its characteristics may be improved.

Keywords: polycrystalline silicon, excimer laser crystallization, Ni-disilicide, Ni-metal-induced lateral crystallization, two-interface grain growth

PACC: 6470K, 6822, 8130

1. Introduction

Low-temperature polycrystalline silicon (poly-Si) film is a promising material for applications in devices, such as solar cells and thin film transistors (TFTs). Solar-cells and TFTs made of this material have high light-absorption index and high mobility of carriers, compared with those made of hydrogenated amorphous silicon (a-Si:H).

Solid phase crystallization (SPC)[1,2] of a-Si is an effective method for the formation of poly-Si with large grain size. However, grains formed by means of SPC not only need high temperature (higher than 600 ° C) and long time (more than 24h), but also tend to include many large-scale crystalline defects, such as twins and stacking faults. For such reasons, the method is not fit for producing high performance TFT on low-cost glass substrate.

To reduce crystallization temperature, metal-induced crystallization (MIC) is a suitable method, which can reduce the temperature to lower than 550°C.[3,4] Applied with an electrical bias, MIC can lower the crystallization temperature down to 400°C.[5,6] For example, with electrical-field-enhanced silicide-mediated crystallization (FE-SMC), a-Si:H thin film can be completely crystallized at 400°C within 30min, and the TFT produced by using the Ni FE-SMC poly-Si thin film exhibits a field effect

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mobility of 76cm^2/V·s.[7]

Grain size of poly-Si prepared by means of excimer laser crystallization (ELC)[8] is relatively large and the concentration of in-grain defects in the resulting materials is very small. Thereby, super performance TFTs, such as high field-effect mobility, low sub-threshold swing value and low threshold voltage, have been prepared. For these reasons, ELC is now a widely used method for preparing high-quality poly-Si thin film on low-cost glass substrate at low temperatures. But there exist some serious problems, such as the laser energy window and poly-Si TFT threshold voltage variation. The laser energy window for forming high-quality poly-Si is narrow. That is, if the applied laser energy density is too small or too large, the size of resulting grains is insufficiently large. In the driving circuits with two poly-Si TFTs in a pixel for organic light emitting diode display, the poly-Si TFT threshold voltage variation results in significant initial output characteristic non-uniformity due to the nature of poly-Si crystal growth.[9,10] Therefore, it is necessary to extend the window of applicable excimer laser energy density and grow high-quality poly-Si to improve TFT characteristics.

In this paper, we prepare the poly-Si thin film by means of $NiSi_2$-assisted ELC method, propose a model for the poly-Si grain growth and also present a discussion.

2. Experimental procedures

Detailed fabrication processes of poly-Si thin film prepared by means of $NiSi_2$-assisted ELC were as follows. On Corning 7059 glass substrate, first a 200-nm-thick silicon oxide as a buffer layer was deposited by low-pressure chemical vapour deposition (CVD). On top of the oxide, a layer of intrinsic a-Si:H thin film with a thickness of 50nm was deposited by plasma-enhanced CVD using a SiH_4/H_2 mixture, with flow rates of 1cm^3/min and 100cm^3/min separately, at a substrate temperature of 250°C and a pressure of 27Pa. After the sample was dehydrogenated in high-purity nitrogen ambient in a quartz container at 450°C for 1h, an about 1.0-nm-thick Ni thin film was deposited by radio frequency sputtering. Then the sample was annealed at 480°C for 20min in vacuum in order to form $NiSi_2$ precipitates. After the remnant of the Ni layer was washed off by nitric acid, the sample was irradiated by XeCl excimer laser (308-nm), with a laser energy density of 300mJ/cm^3 and in a 90% overlapping ratio, in vacuum at 300°C. By the above processes, sample 1# was prepared, and another two samples 2# and 3# were prepared under slightly different conditions in order to compare with sample 1#. When the process proceeded to anneal at 480°, samples 2# and 3# were prepared for about 12h and 20min respectively. Their processes are consistent with the conventional Ni-MIC. Raman scattering, x-ray diffraction (XRD) and scanning electron microscopy (SEM) were applied to characterize the resulting poly-Si thin film.

3. Results and discussion

Raman spectra of the samples are shown in Fig.1. The spectrum of sample 3# shows a broad structure with a full width at half maximum (FWHM) of about 20cm^{-1}, and can be described by the overlapping of two Gaussian peaks at 513cm^{-1} and 480cm^{-1}. It indicates that the film consists of microcrystalline phase of silicon and a-Si. Spectra of samples 2# and 1# have peaks centred at 520cm^{-1} with FWHM of 8.6cm^{-1} and 7.4cm^{-1} respectively. The FWHM values of samples 2# and 1# are larger than the 4.5cm^{-1} obtained from single-crystal silicon, which indicate that the films consist of poly-Si grains. And the FWHM value of the sample 1# is smaller than that of the sample 2#, indicating that its average grain size is larger than that of the sample 2#.

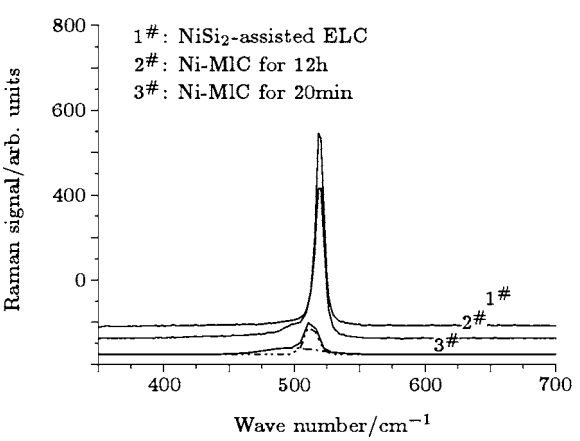


Fig.1. Raman spectra of samples 1#, 2# and 3#.

Figure 2 shows XRD patterns of samples 1#, 2# and 3#. A broad crystalline (220) peak has been observed in the sample 3#. It indicates that the microcrystalline silicon has formed and the result is consistent with that of Raman spectrum. The crystalline silicon peaks at d=3.14Å (111), d=1.92Å (220) and d=1.64Å (311) appear in sample 1#, and its intensity is higher than that of sample 2#, indicating that sample 1# has higher crystallinity.

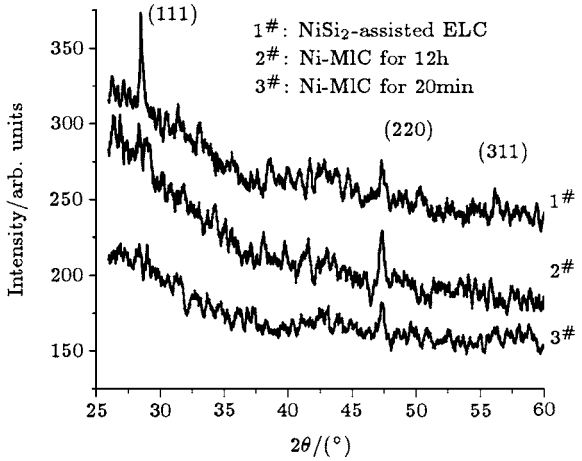


Fig.2. XRD patterns of samples $1^{\#}$, $2^{\#}$and $3^{\#}$.

In Fig.3, micrograph (a) shows the needle-shaped random poly-Si grains prepared by means of conventional Ni-MIC,[11] micrograph (b) shows the morphology of sample $2^{\#}$ after Secco's etching, and (c) shows the morphology of sample $1^{\#}$ after Secco's etching. It can be seen that sample $1^{\#}$ also shows needle-shaped grains. But a clear difference between photos (a) and (c) is that the grains in (c) mostly extend along the same orientation, as indicated by arrows.

According to experimental results of SEM, a grain growth model, named two-interface grain growth, has been proposed. That is, an additional grain growth interface to contrast with conventional ELC has formed, which consists of $NiSi_2$ precipitates and a-Si. Figure 4(a) shows the schematic diagram of this model. $NiSi_2$ precipitates can be very important in the crystallization process. They have the same crystal structure (the fluorite type) and only a small lattice mismatch (0.4%) with c-Si.[4] Figure 4(b) shows the orientations of $NiSi_2$ precipitates. The shaded area region in each precipitate represents the face on which MILC starts. The arrow indicates the normal direction to the face, along which grain growth takes place. It also indicates that [110] is favourable but [100] and [111] are unfavorable, because [100] and [111] oriented precipitates have the normals which will intersect either top or bottom of the surface for MILC. Moreover, Yunosuke and Hiroshi [12] have studied the initial stage of the interfacial

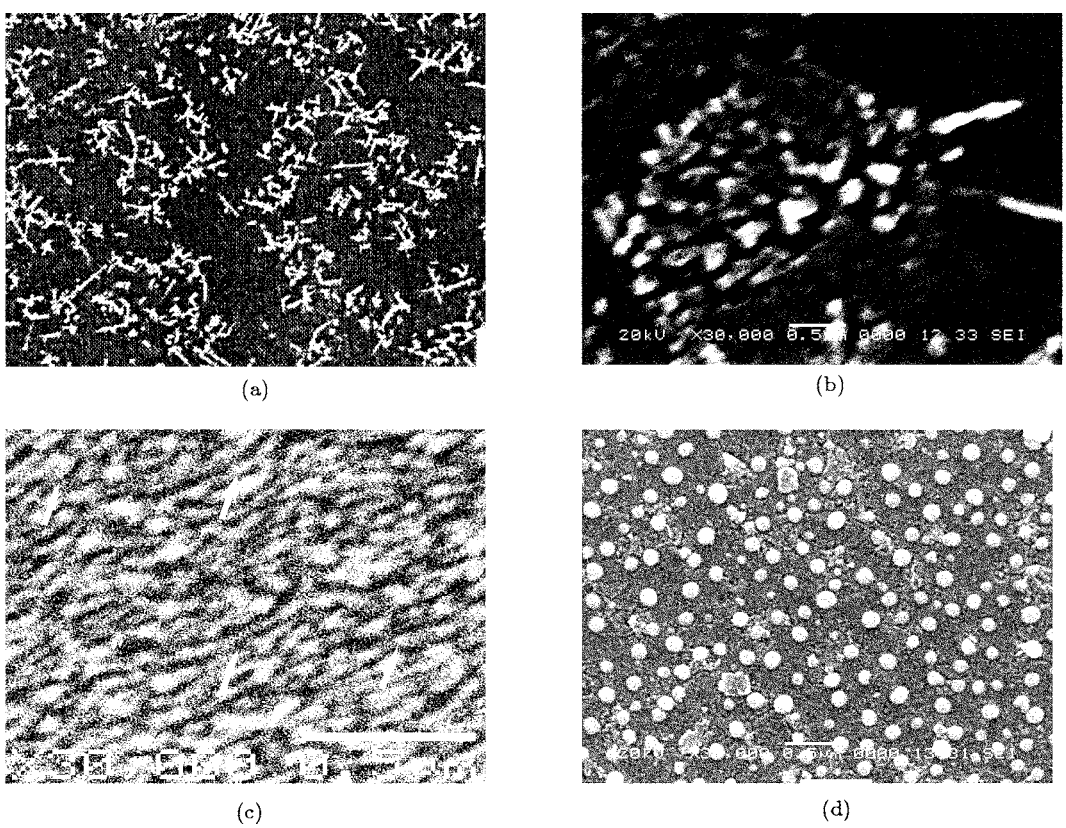


Fig.3. SEM images of poly-Si thin films: (a) the needle-shaped poly-Si, (b) sample $2^{\#}$ after Secco's etching, (c) sample $1^{\#}$ after Secco's etching and (d) poly-Si grains prepared by means of $NiSi_2$-assisted ELC but without the process of heat-treating to form $NiSi_2$.

reaction between Ni and a-Si:H. It shows (Fig.3 in Ref.[12]) the various characteristic temperatures for the formation of phases of Ni-silicide. When annealed up to 470°C, the end phase of Ni-silicide, octahedral $NiSi_2$, appears with its XRD peak intensity of (220) stronger than that of (111). So the broad peaks in Raman spectrum and XRD pattern of sample $3^{\#}$ indicate that $NiSi_2$ precipitates are formed. They are very important for ELC carried out successively. If the dehydrogenated a-Si with a thin layer of Ni was not heat treated, the formed Ni thin film would melt and agglomerate into drops under laser irradiation, as shown in Fig.3(d).

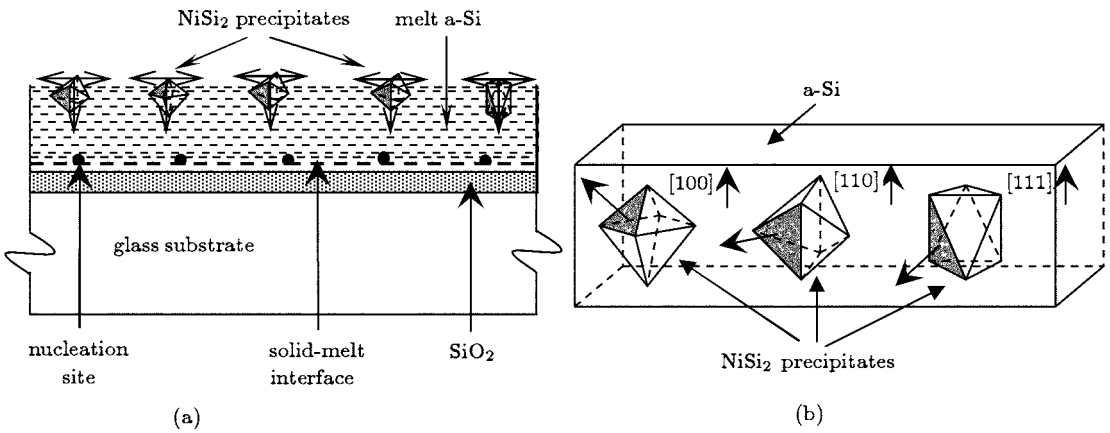


Fig.4. (a) The schematic diagram of the crystallization of a-Si by means of $NiSi_2$-assisted ELC; (b) the schematic diagram of orientations of $NiSi_2$ precipitates favourable ([110]) and unfavorable ([100], [111]) for MILC.

In the grain growth model of conventional ELC, it is divided into three grain growth regions according to various excimer laser energy densities delivered to a-Si thin films, which were observed by Im *et al.*[13−15] Figure 5 shows the schematic diagram of crystallization of a-Si by means of ELC. There are also three grain growth regions in the two-interface grain growth, but the processes of grains growing are different from that by means of ELC. In low-energy density region, grain growth process is dominated by $NiSi_2$ precipitates acting as seeds. As the melt depth is less than the film depth, a thin layer of poly-Si grains is formed laterally. As laser energy increases to near-complete-molten region, $NiSi_2$ precipitates and the surviving residual solids in the two interfaces act as seeds, where grain growths proceeds simultaneously. In our early experimental results,[16,17] laser energy density for the near-complete-molten region was about 300mJ/cm^2, which was also adopted in this work. The last region is complete-molten or high-energy-density region. For the too high laser energy density, the thin film will become amorphous again, and the grain size decreases to generally no more than a few tens of nanometres. According to the above analysis, on account of the existence of $NiSi_2$ precipitates, a wide laser energy window is needed to crystallize a-Si in comparison with that in conventional ELC.

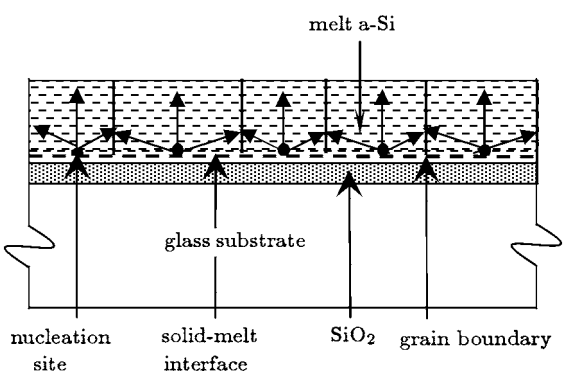


Fig.5. The schematic diagram of crystallization of a-Si by means of conventional ELC.

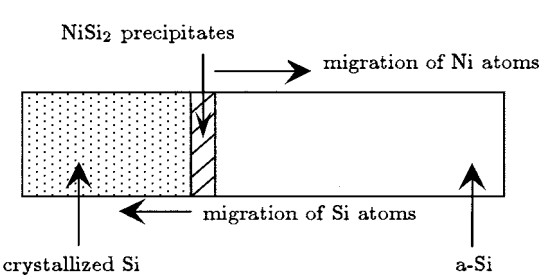


Fig.6. The schematic diagram of crystallization of a-Si by means of Ni-MILC.

Figure 3(c) shows the morphology of needle-shaped poly-Si grains grown with $NiSi_2$ precipitates

as seeds, and most of the grains are in the same orientation. If such grains are utilized to prepare TFT and their preferential orientation is along the channel of TFT, the improvement of TFT characteristics is expected. Although the reason is not clear, the improvement is related to the excimer laser scanning mode, such as laser overlapping ratio, laser frequency and the moving way of laser facula. The mechanism must be different from that of Ni-MILC, because the grain growth time by means of $NiSi_2$-assisted ELC is much shorter than that by means of Ni-MILC which needs several hours through Ni atoms migration. Figure 6 shows the crystallization process of a-Si by migration of Ni and Si atoms,[4] demonstrating that $SiNi_2$ precipitates only act as seeds in the process of $NiSi_2$-assisted ELC.

4. Conclusion

Poly-Si thin film has been prepared by means of $NiSi_2$-assisted ELC. Grains with needle shape and most of a uniform orientation were prepared with $NiSi_2$ precipitates as seeds. It is expected that the grains can improve TFT characteristics, such as I-V and threshold voltage. According to the experimental results, a model, named two-interface grain growth, is proposed, which is different from that of conventional Ni-MILC and ELC. In the new model, Ni atoms do not migrate and an additional grain growth interface is formed in the crystallization process. Grain growth processes dependent on various laser energy densities have been discussed. It is predicted that a wide laser energy window can be realized. The mechanism to form such grains is currently under investigation.

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