

Enhanced Crystallization of Amorphous Si Using viscous Ni Solution and Microwave Annealing

Jin Hyung Ahn, Ji Hye Eom, and Byung Tae Ahn, *Member*

Abstract

A viscous Ni solution was coated over amorphous Si thin film for evenly spread of Ni metal source. The Ni s . . . prepared by dissolving $NiCl_2$ into 1N HCl and mixing with propylene glycol. $NiCl_2$ and Ni were deposited on the amorphous film after oven dry and they enabled to obtain a uniform crystallization. The crystallization using the viscous Ni solution was a Ni-silicide mediated process, the same process used with Ni metal layer. The crystallization temperature was lowered to 480 °C by the synergy effect of silicide-mediated crystallization and microwave-induced crystallization. Lateral crystallization was also enhanced such that the velocity of lateral crystallization by microwave annealing became faster than by furnace annealing.

Keywords : Crystallization, polycrystalline silicon, metal solution microwave annealing.

1. Introduction

Polycrystalline Si (poly-Si) thin films used in displays are generally fabricated by crystallizing amorphous Si (a-Si) thin film precursors. Among the crystallization methods, solid phase crystallization (SPC) in which a-Si films are annealed without melting is simpler and easier than excimer laser annealing (ELA) in making uniform poly-Si films. But the SPC process generally takes a long time to crystallize a-Si films at 600 °C, which is too a high temperature for large area glass substrates. There have been many studies done to lower the crystallization temperature of a-Si films. One of the methods is annealing a-Si films with a thin metal layer on its surface [1-5]. Sohn reported that the crystallization was enhanced by spin coating of metal solutions [6, 7]. Lee fabricated high-performance thin film transistors (TFTs) by laterally crystallizing the channel area from the source/drain area on which 5 Å thick Ni was deposited by sputtering [8]. Yoon reported that a-Si films could be crystallized at 500 °C in 20 h using Ni solution [9]. Another method of enhancing crystallization is annealing a-Si films with microwave heating. Lee reported that the crystallization temperature was much reduced by annealing a-Si films with microwave heating even without metal deposition [10, 11].

In this study, amorphous Si thin films on which $NiCl_2$ and Ni were deposited from a viscous Ni solution were crystallized in a furnace or a microwave annealing system. The viscous Ni solution prepared by dissolving $NiCl_2$ in 1N HCl and mixing it with propylene glycol was applied to overcome the nonweting nature of the Ni solution with only diluted acid. The coating of viscous Ni solution enabled the uniform crystallization and further enhanced the crystallization of a-Si film with the synergy effect caused by microwave annealing.

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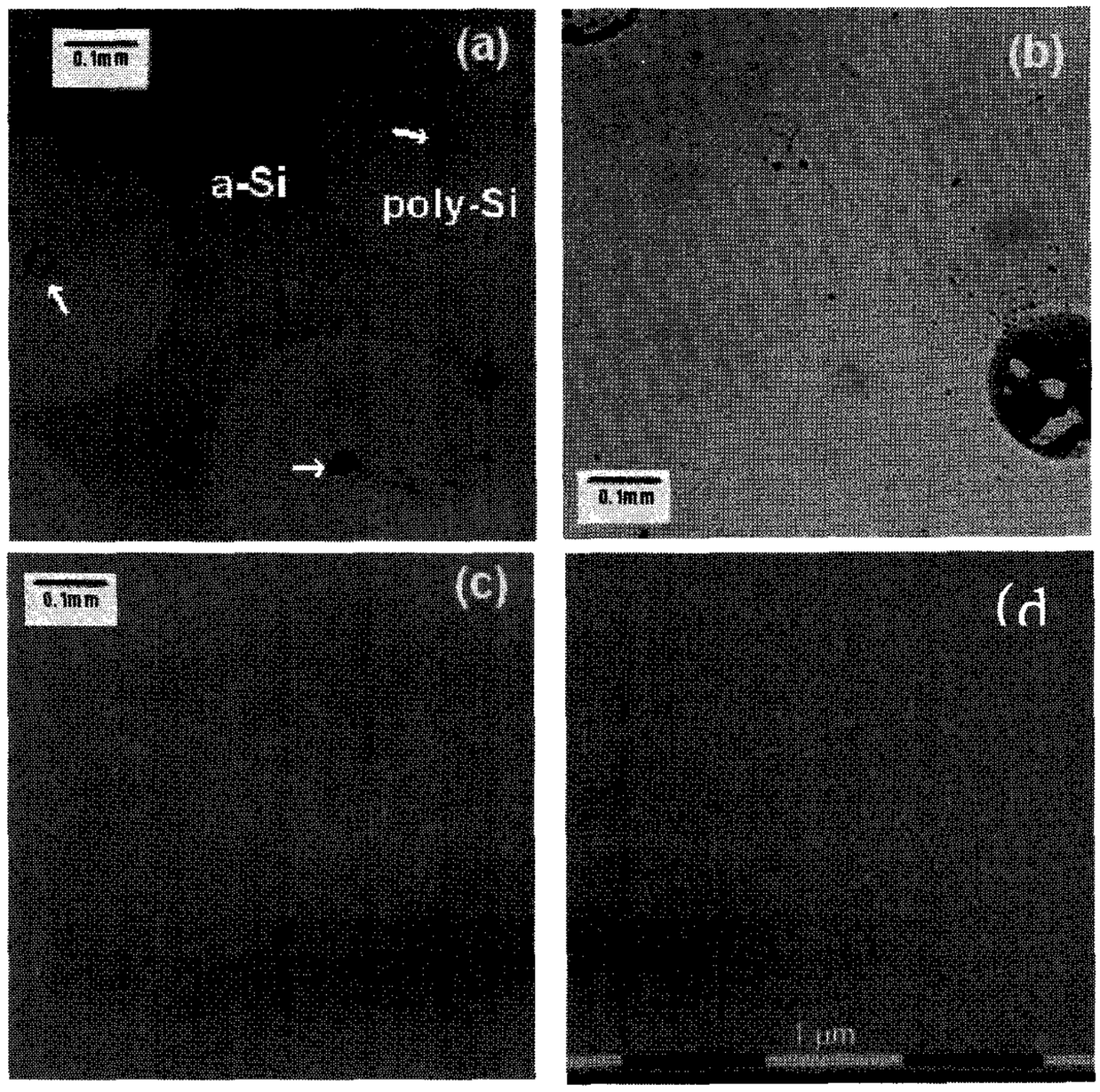

Fig. 1. Surface morphology of Si films annealed at 500 °C for 10h. Ni was applied from (a) 1,000 ppm, (b) 100,000 ppm $NiCl_2$ solution with 1N HCl only and from (c), (d) 0.1M $NiCl_2$ solution with 1N HCl+PG.

2. Experiments

100 nm-thick a-Si films were deposited on oxidized Si wafers by LPCVD using Si_2H_6 at 530 °C. The a-Si films were cleaned in boiling H_2SO_4+H_2O_2 solution and dipped in diluted HF solution to remove oxide on the film surface. Viscous Ni solution was prepared by dissolving $NiCl_2$ in 1N HCl and mixing it with propylene glycol. The volumetric ratio of 1N HCl and PG was fixed to 1:4. Ni solution was spin-coated at 5000 rpm and dried at 230 °C. After that, the a-Si film was annealed in a microwave system or in a conventional tube furnace. The frequency of the microwave was 2.45 GHz and about 300 W of the microwave power was consumed to maintain the Si wafer at 500 °C.

The surface morphology of annealed Si films was observed using optical microscope and scanning electron microscopy (SEM). For the identification of the coated layer and its chemical variation Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS) analysis were conducted. The top surface of the samples was sputtered off before the XPS analysis to determine the bulk composition of the coated layer. The microstructure of the Si film was observed using transmission electron microscopy (TEM), and the crystalline fraction in the Si films was measured using X-ray diffraction (XRD) and Raman spectroscopy.

To investigate the lateral crystallization behavior, SiO_2 mask layer was deposited and patterned on a-Si films before Ni solution coating. After drying the Ni solution, the samples were annealed in a microwave system or in a furnace. The depth of the lateral crystallization beneath the SiO_2 mask was observed using optical microscope.

3. Results and Discussion

Figure 1 shows the optical microscopic images of the surfaces of LPCVD Si films after annealing at 500 °C for 10 h with nonviscous coating of (a) 1,000 ppm and (b) 100,000 ppm Ni solutions, and (c) viscous 0.1 M Ni solution. Figure 1d shows the SEM planar image of the film depicted in Fig. 1c. Lumps of adsorbate are seen in Fig. 1a (arrows). The lumps originated from the agglomeration of the solute as the droplets of Ni solution

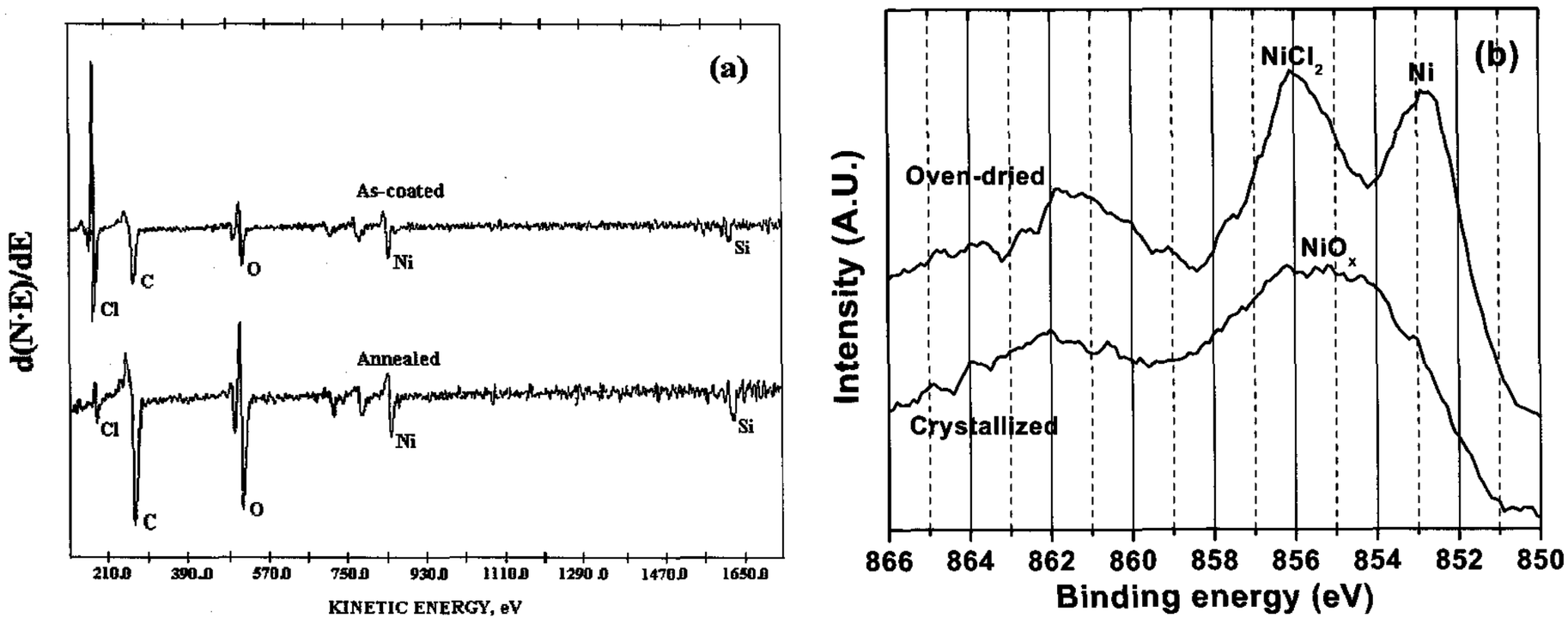

Fig. 2. AES spectra (a) and Ni 2p3/2 XPS spectra (b) of the a -Si surface for oven-dried sample after coating viscous $NiCl_2$ solution and for the poly-Si film annealed at 530 °C for 5 h in Ar.

dried. The nonviscous acid solution resulted in uncontrollable forms of droplets because the Si surface was hydrophobic and Ni with the electronegativity not larger than that of Si could not be effectively adsorbed onto the Si surface. So, the a-Si film around the lumps was crystallized, while the other region remained amorphous. The coating of nonviscous acid solution resulted in a non-uniform and irreproducible deposition of $NiCl_2$, causing a non-uniform crystallization. With the increase in the Ni solution concentration, the lumps became larger and small spots of crystallized region were also detected in amorphous matrix (Fig. 1b). Thus, it can be said that it is difficult to uniformly crystallize a-Si films by coating of nonviscous Ni solution. By employing a viscous Ni solution, a uniform film instead of droplets is coated. No lumps of adsorbate are detected after drying the film even in SEM investigation (Fig. 1d). And sufficient amount of Ni is uniformly supplied from the coated layer such that Ni silicide enhanced crystallization can be uniformly achieved, as shown in Fig. 1c. Employing the viscous solution enabled us to produce a uniform and reproducible film. Employing the viscous Ni solution helped in clearly overcoming the limitation that of the crystallization that employs the nonviscous metal solution.

For the identification of the coated layer and its chemical, AES and XPS analysis were conducted. Figure 2 shows the AES spectra (a) and Ni 2p3/2 XPS spectra (b) of the coated layer of the oven-dried and crystallized (at 530 °C for 5 h) Si films. In Fig. 2a, after crystallization the peak-to-peak intensity of Cl was remarkably reduced while that of O increased (Fig. 2a). In the oven-dried film in Fig. 2b, the Ni 2p3/2 peak is located at 856.1 eV corresponding to $NiCl_2$ and 852.7 eV corresponding to Ni. The peak near 862 eV is a satellite peak. Ni 2p3/2 peak shifted and broadened to lower energies of 855.8 eV and 854.4 eV, which correspond to Ni_2O_3 and NiO, respectively. So it can be said that $NiCl_2$ and Ni are deposited on the a-Si surface and they react with oxygen to form NiO_x during crystallization.

Figure 3 shows the TEM microstructures of Si films annealed at 450 °C for 5 h (Fig. 3a) and at 500 °C for 10 h (Fig. 3b). 0.1 M Ni solution was used for Fig. 3a and 0.001 M Ni solution was used for Fig. 3b. Square-shaped precipitates are seen in a-Si matrix in Fig. 3a and a dark plate with the thickness of about 6 nm is seen on the edge of a crystalline Si grain in Fig. 3b. Ni was detected in the electron dispersive spectroscopy (EDS) analysis of the square-shaped precipitates and the plate, while Cl could not be observed. This indicates that the precipitates and plate are compounds of Ni and Si, i.e., a Ni silicide. Hayzelden et. al. studied the mechanism of Ni silicide mediated crystallization with *in situ* TEM observation [12-14]. They reported that Ni reacts with Si to form $NiSi_2$ precipitates and crystalline Si nucleates at the surface of the $NiSi_2$ precipitates. The crystalline nuclei grew as a result of the addition of Si from a-Si through $NiSi_2$ precipitates. As the result, the $NiSi_2$ precipitates

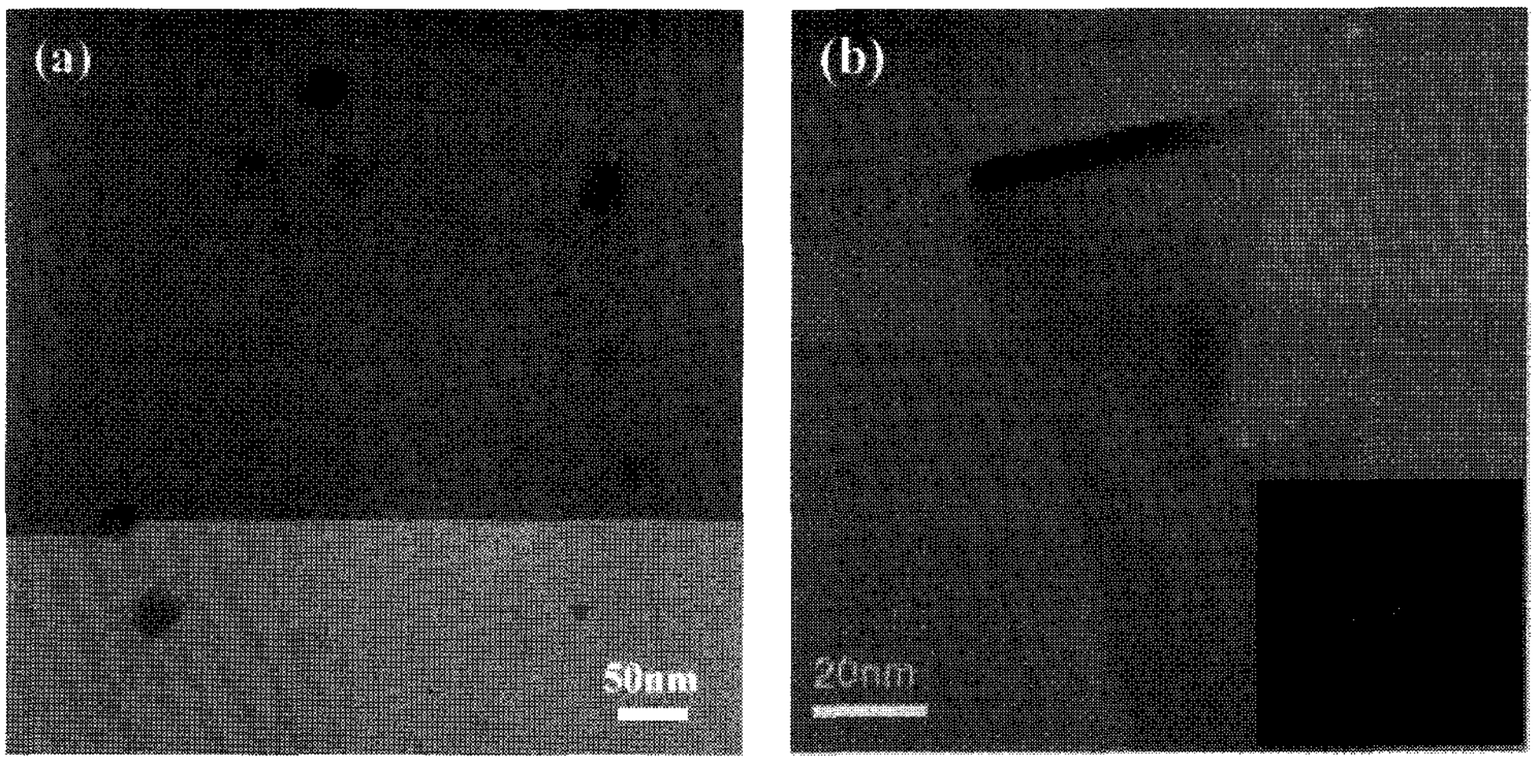

Fig. 3. TEM microstructures of Si films annealed (a) at 450 °C for 5 h and (b) at 500 °C for 10 h. Ni source was deposited from (a) 0.1 M and (b) 0.001 M viscous Ni solution.

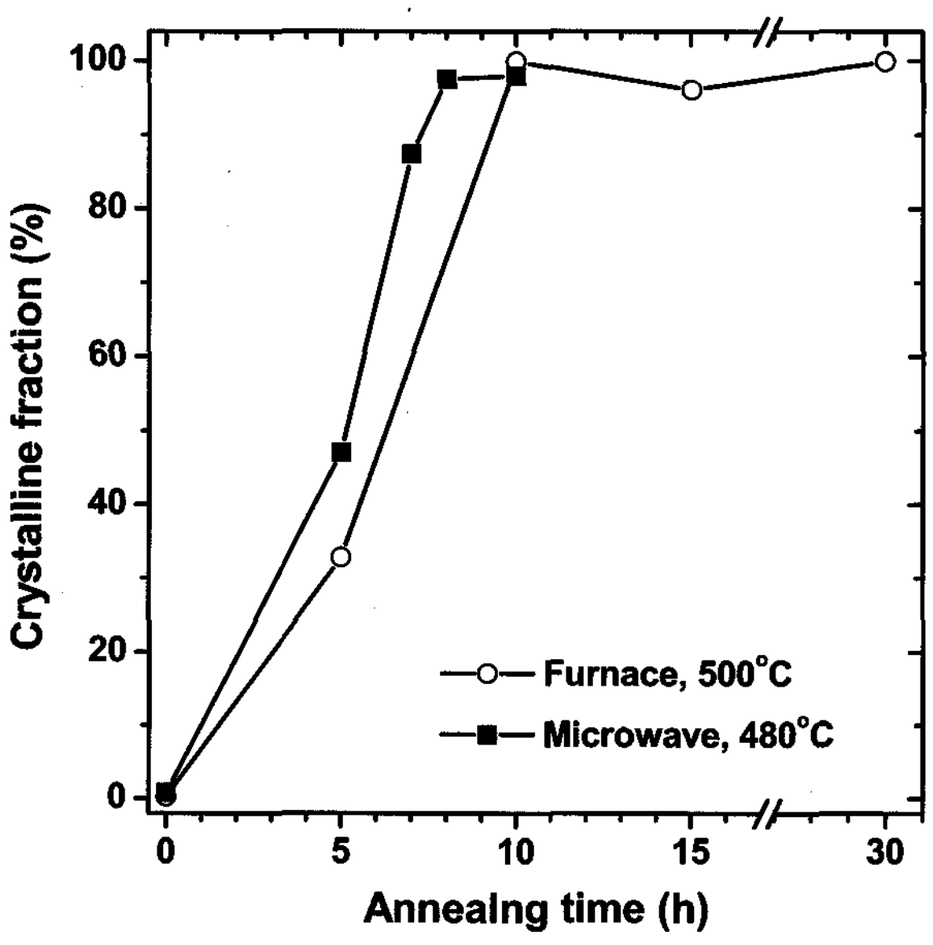

Fig. 4. Crystallization behaviors of $NiCl_2$ and Ni deposited a-Si films annealed in a furnace and in a microwave system.

migrate through a-Si region and needle-like grains grow. In Figs. 3a and 3b, the shape of the precipitates aresimilar to those of $NiSi_2$ precipitates observed in the Ni silicide mediated crystallization, using Ni metal layer. Moreover, the selected area diffraction pattern from the crystalline Si grain and $NiSi_2$ plate coincide well with each other (inset of Fig. 3d). This indicates that the phase on the edge of the crystalline Si grain is $NiSi_2$ which is almost isomorphic and has very small lattice mismatch with crystalline Si. From these results, it can be said that the crystallization using viscous Ni solution is also $NiSi_2$ mediated process.

Figure 4 shows the crystallization behaviors of a-Si films coated with 0.005 M solution and annealed in a tube furnace and in a microwave system. It took about 30 h to fully crystallize intrinsic a-Si films at 600 °C. The a-Si film coated with $NiCl_2$ and Ni from the viscous Ni solution was fully crystallized in 10 h in the furnace at a temperature of 500 °C and fully crystallized in 8 h in the microwave annealing system at a temperature of 480 °C The use of both viscous metal solution and microwave annealing enabled us to lower crystallization temperature from 600 °C down to 480 °C.

Lee first reported that the crystallization of intrinsic a-Si films could be enhanced with microwave heating [10]. In the paper, he also reported the fast evolution of hydrogen which is originally contained in the a-Si film during the deposition. The fast evolution of hydrogen and the enhanced crystallization may be due to electromagnetic field effect that increases the atomic mobility, especially Ni in $NiSi_2$ precipitates. The crystallization occurs through nucleation and growth process. In intrinsic a-Si, nucleation is the dominant factor for crystallization. The nucleation may start with the formation of $NiSi_2$ precipitates which depends on the amount of $NiCl_2$ and Ni coating on Si surface. The enhanced crystallization by microwave annealing suggests that the reaction between Ni source and a-Si to form $NiSi_2$ is enhanced by the increase of Ni mobility or Si mobility. Detailed discussion on the nucleation is beyond the scope of this paper.

The enhancement of microwave annealing can also be clearly seen through the lateral crystallization of a-Si films using the viscous Ni solution. Lateral

crystallization is the phenomenon that the poly-Si region precrystallized by silicide mediated process propagates to the intrinsic a-Si region with no Ni on it because oxide mask prevents direct contact between Ni and a-Si film. The precrystallized region acts as the seed of grain growth. Lee and Joo fabricated high-performance thin film transistors by the lateral crystallization of the channel area from the source/drain area on which 5 Å thick Ni metal was deposited by sputtering [8], and several researchers investigated lateral crystallization [15-17].

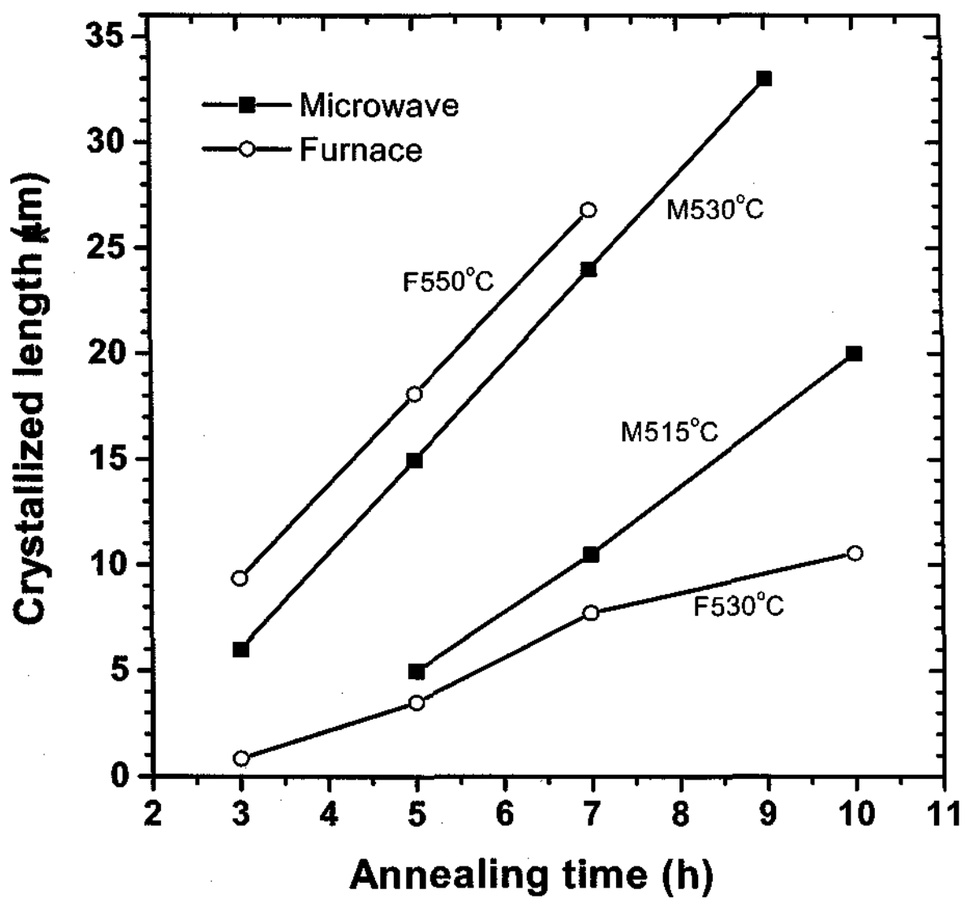

Fig. 5. Lateral crystallization behavior with microwave and furnace annealing at various annealing temperatures.

Figure 5 shows the lateral crystallization behavior with microwave annealing and furnace annealing at various annealing temperatures. The length of lateral crystallization with microwave annealing is larger than that with furnace annealing. At 530 °C, the crystallized length after 7 h by microwave annealing was 24.0 μm while that after 7 h by furnace annealing was 7.7 μm. The velocity of lateral crystallization increased from 1.9 μm/h to 4.5 μm/h by microwave annealing. The mechanism of crystallization process consists of nucleation and growth. The lateral crystallization process is the lateral growth process of poly-Si that is already grown by $NiSi_2$ in the unmasked Si film region. The velocity of lateral crystallization is the velocity of lateral grain growth. Table 1 summarizes the time necessary for 10 μm lateral crystallization and the velocity of lateral crystallization in furnace and microwave annealing system. In Table 1, we can see, qualitatively, that the lateral crystallization is enhanced with microwave annealing even though the quantities themselves may depend on experimental conditions. The velocity of lateral crystallization is believed to be related to the Ni diffusion in $NiSi_2$, considering that the of Ni silicide mediated crystallization reported by Hayzelden with in-situ TEM observation. Si grain grows as the $NiSi_2$ precipitate on its edge migrates toward amorphous matrix [13,14]. By lateral crystallization, $NiSi_2$ precipitates exist in the middle of the channel of TFTs [18].

The activation energies of the velocity of lateral crystallization, which were racted from the Arrehnius plot [ln(velocity) vs. 1/kT], were 2.12 eV for furnace annealing and 1.55 eV for microwave annealing. The lowered activation energy indicates that the lateral growth mechanism in microwave system is different from that in farnace. The microwave annealing not only supplies heat to Si substrate but also enhances the atomic mobility in $NiSi_2$ precipitates and at $NiSi_2$/a-Si interface. The enhanced mobility may be the result of microwave AC field effect.

The enhanced lateral crystallization and the reduced activation energy in Fig. 5 indicates that microwave

TABLE 1. The time to 10 μm lateral crystallization and the velocity of lateral crystallization in furnace and microwave system.

Annealing Temperature (℃)	Time to 10μm Crystallization (h)		Velocity (μm/h)	
	Furnace	Microwave	Furnace	Microwave
500	27.5	10.6	0.68	1.95
515	14.6	6.7	1.12	3.01
530	9.3	3.9	1.43	4.50
550	3.1	2.05	4.37	8.07

annealing clearly enhance the growth of poly-Si grains with different or modified diffusion mechanism. In silicide-mediated crystallization with microwave annealing, both nucleation and growth process affect the enhanced crystallization. The enhancement of growth process was clearly seen in Fig. 5. The enhancement of the growth of Si nuclei may be a reason of the enhanced crystallization of a-Si films, shown in Fig. 4. But more detailed work on nucleation process should be further studied to clearly explain Fig. 4.

4. Conclusions

A viscous Ni solution was applied on a-Si film for uniform coating of Ni metal source. $NiCl_2$ and Ni metal were deposited on a-Si films from the viscous solution. Crystallization was also a Ni silicide mediated process. Combining silicide-mediated crystallization and microwave induced crystallization further enhanced crystallization of a-Si films that LPCVD a-Si films deposited from Si_2H_6 gas was fully crystallized at 480 °C in 8 h. Lateral crystallization was also enhanced with the microwave annealing and the velocity of lateral crystallization with microwave annealing was faster than that with furnace annealing.

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