Microwave-Enhanced Low-Temperature Crystallization of Amorphous Silicon Films for TFTs

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Abstract

Microwave has been utilized for low-temperature crystallization of amorphous Si films. Microwave annealing lowered the crystallization temperature and shortened the annealing time. The combination of Ni and microwave applications on a-Si films further enhanced the crystallization. The enhancement was due to both reduced nucleation activation energy and growth activation energy.

1. Introduction

The solid phase crystallization of a-Si films is one of the possible methods to prepare polycrystalline Si films. The SPC process takes long time (> 10h) to crystallize a-Si films at 600 °C that is too high for large-area glass substrates. Many methods have been reported to lower the crystallization temperature. For example, metal solutions [1,2] and metal layers [3] were applied on a-Si films, lowering crystallization temperatures. The metal-induced crystallization occurs mainly reducing the activation energy of Si diffusion through intermediate phases such as silicide or amorphous interlayers. By microwave annealing, it is possible to lower the crystallization temperature even without metal addition [4,5]. The microwave annealing is a physically enhanced process by the interaction of microwave field and mobile species, while the metal-induced crystallization is a chemically enhanced process by lowering the diffusion energy barrier through membranes. The combination of metal induced crystallization and microwave enhanced crystallization can further enhances the crystallization. In this case, we may reduce the amount of metal application to a-Si films so that the metal contamination can be reduced.

This paper presents the crystallization behaviors of both intrinsic a-Si films and Ni-coated a-Si films with microwave application. The electrical properties of poly-Si TFTs by microwave annealing were comparable to that of poly-Si TFT furnace annealing.

2. Experiments

A-Si films were prepared by LPCVD at 545 °C using SiH_4 gas or at 530 °C using Si_2H_6. The a-Si films were cleaned in a boiling H_2SO_4+H_2O_2 solution and dipped in diluted HF solution to remove oxide on the surface. For silicide mediated crystallization (SMC), Ni was supplied on the a-Si films in the form of $NiCl_2$ from a Ni solution prepared by dissolving $NiCl_2$ in the mixture of 1N HCl + propylene glycol. For silicide mediate lateral crystallization (SMLC), SiO_2 mask layer was deposited and patterned prior to the Ni coating.

Specimens prepared as the above were annealed in a microwave annealing system in nitrogen. The system consists of a microwave generator and an annealing chamber. Microwave with 2.45 GHz frequency was supplied from the microwave generator to the chamber through a waveguide. Specimens are put on a tray made of Si wafer and the temperature of the Si tray was measured with a thermocouple.

The crystalline fraction in the Si films was measured with (111) X-ray diffraction intensities and SEM images observed after etching off a-Si region with Si defect etchant (1.75M:1:100 CrO_3+ 49%HF+H_2O). The length of the lateral crystallization beneath SiO_2 mask layer was measured using optical microscope. The microstructural evolutions during crystallization were observed using SEM and TEM.

3. Results

Figure 1 shows the crystalline fraction of SiH_4 LPCVD a-Si films as a function of annealing time by microwave annealing at 550, 530, and 500 °C. The microwave annealing clearly enhances the solid-phase crystallization process. The time dependence

of the crystalline fraction can be expressed by the Avrami equation [7],

$$X_c = 1 - \exp[-\{(t - t_0)/ t_c\}^n], \qquad (1)$$

where, t_0 is the incubation time, t_c is the characteristic time, and n is the exponent depending on the crystallization mechanism. Here, t_0 denotes the time before nucleation occurs and the inverse of t_0 is reported to be proportional to the nucleation rate.

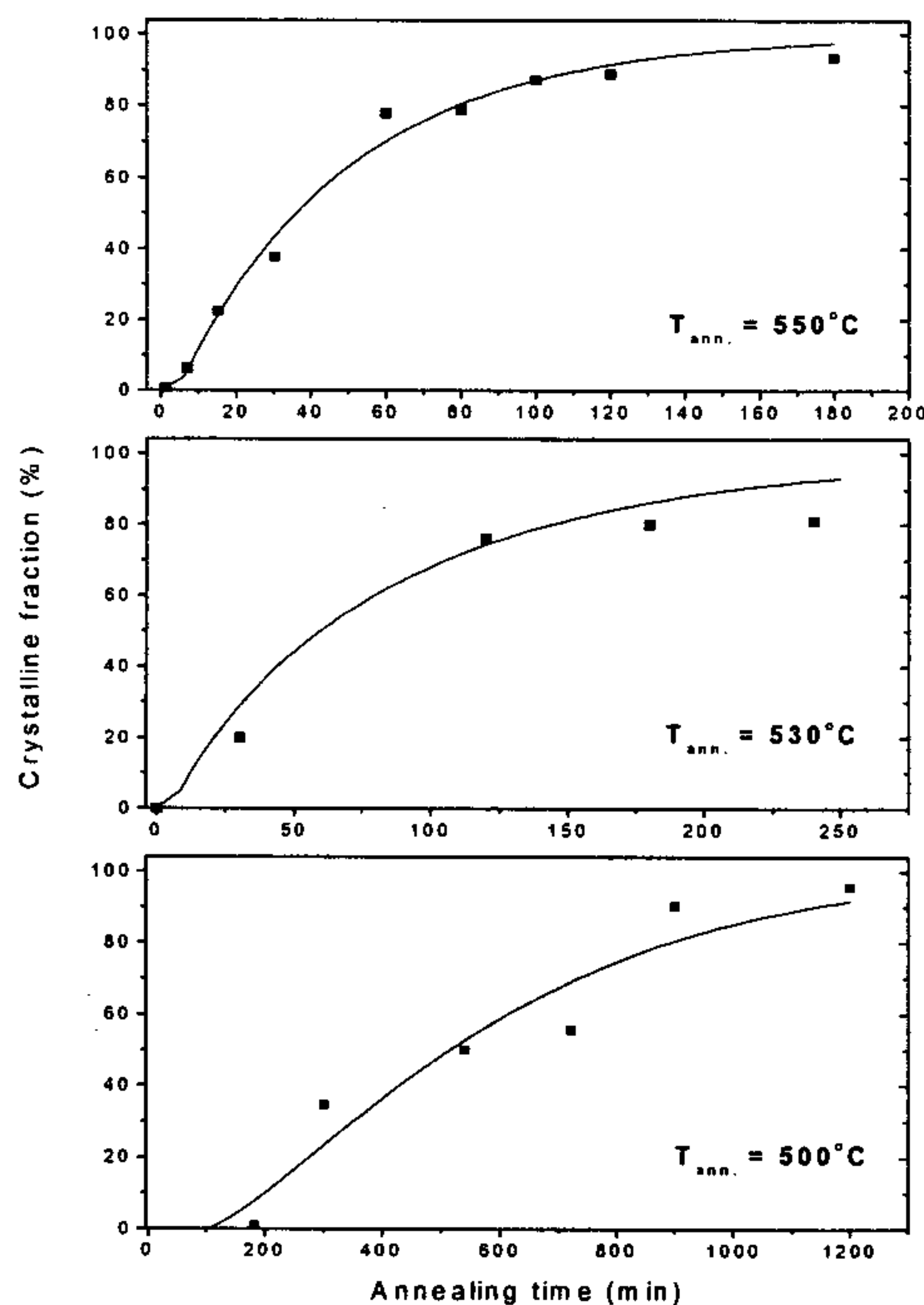

Figure 1. Crystalline fraction of SiH_4 LPCVD a-Si films as a function of microwave annealing time.

The solid lines in Fig. 1 are fitted lines using the Avrami equation and t_0, t_c, and n are obtained from the fitted curves. The t_0 values by microwave annealing at 550, 530, and 500 °C are 4.5 min, 5.5 min, and 1 h 37 min, respectively. Those by furnace annealing are 2 h at 560 °C and 17 h at 530 °C, respectively. The activation energy of t_0 obtained from the Arrhenius plot was 3.53±1.2 eV, while the value observed in conventional furnace annealing is 3.9 eV. The activation energy of t_0 represents the activation energy of nucleation rate.

Figure 2 shows the SMC behavior of $NiCl_2$ coated on Si_2H_6 LPCVD a-Si films with microwave and furnace annealing at 460, 480 and 500 °C. Solid lines are the results of fitting the behaviors with the Avrami equation. Note that the SMC process was enhanced at all annealing temperatures with microwave annealing. At 480 °C, the crystallization was completed after 7 h by microwave annealing, while the crystallization was completed after 15 h by furnace annealing. Thus, we can see here that the enhanced crystallization with Ni application was further enhanced with microwave annealing. So far it can be said that 480 °C is considered as a lowest crystallization temperature in reasonable time frame.

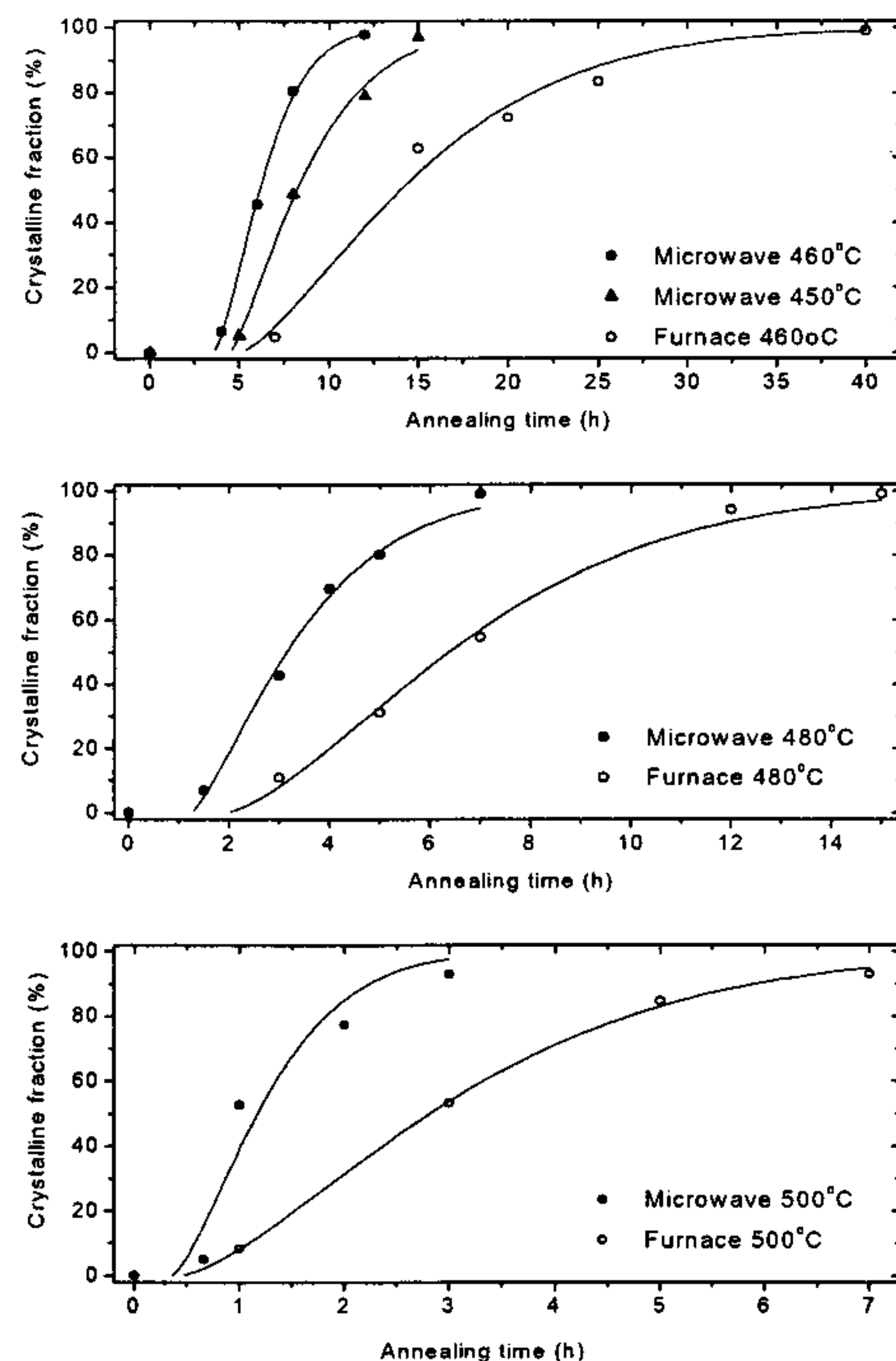

Figure 2. Crystallization behavior of $NiCl_2$ coated Si films with microwave and furnace annealing.

The crystallization behavior in this work was also fitted well with Avrami equation with the exponent value between 1.3 and 1.5. The t_0 values by microwave annealing at 450, 460, 480 and 500 °C are 4.46 , 3.34 , 2.52 and 1.06 h, respectively. Those by furnace annealing at 460, 480 and 500 °C are 5.02, 1.90, and 0.45 h, respectively. The activation energies of SMC in furnace and microwave annealing are 3.05 and 2.50 eV, respectively. Since the a-Si films are prepared from Si_2H_6 gas, the activation energy is expected to be slightly higher that that from a-Si films deposited from Si_2H_6 gas. Note that the microwave annealing reduced the nucleation activation energy.

So far our results are described in relation to nucleation activation energy. It is expected that the microwave annealing also enhance the growth rate. But it is difficult to isolate the growth rate from the crystallization fraction because it contains both

nucleation and growth process. The t_c in the Avrami equation indicate the statistical view of complete crystallization with 67% of crystallization. Beyond t_c, there might be significant impingement among grains. The activation energies of t_c in intrinsic a-Si film and Ni-coated a-Si film by microwave annealing are 2.8±0.5 and 1.39 eV, respectively. Since most of the heterogeneous nucleation occurs at the early stage of nucleation, these energies are related to growth activation energy to some extent even though it is not exact.

Figure 3 shows the SMLC behavior of Si_2H_6 LPCVD a-Si films by microwave annealing and furnace annealing at various annealing temperatures. The SMLC starts earlier and grows faster by microwave annealing than furnace annealing. Note that the microwave annealing clearly enhanced the SMLC process. At 530 °C, the length of the lateral crystallization after 7 h with microwave annealing was 24.0 μm while that with furnace annealing was 7.7 μm. The lateral crystallized length with microwave annealing was generally three times larger than that with furnace annealing.

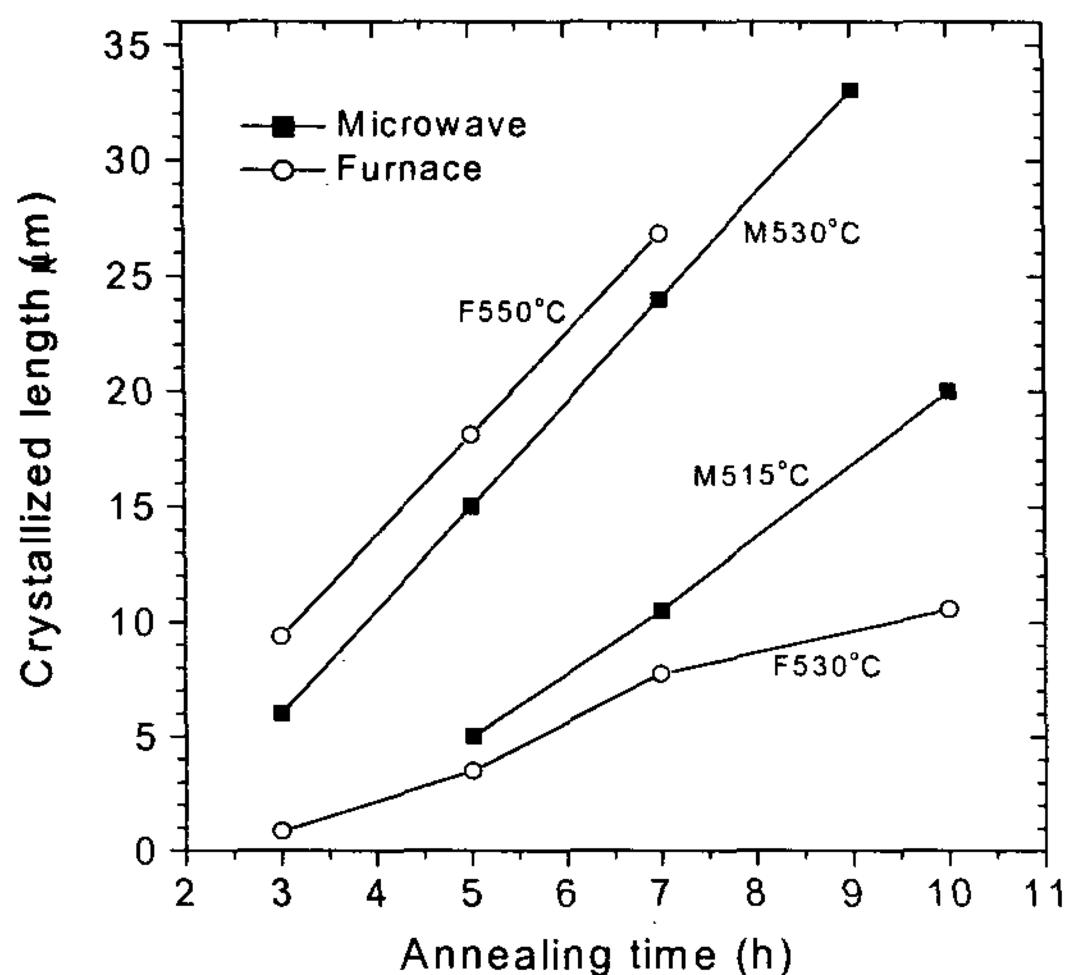

Figure 3. Lateral crystallization behavior with microwave and furnace annealing at various annealing temperatures.

Figure 4 shows the Arrhenius plot of the velocity of lateral crystallization at various crystallization temperatures. The slope of the plot means the activation energy of the velocity of lateral crystallization. The activation energies by microwave annealing and with furnace annealing are 1.55 and 2.12 eV, respectively. The crystallization activation energy of intrinsic a-Si in Fig. 2 was 2.8 eV. Since the heterogeneous nucleation is almost completed at edge of SMC boundaries at the early stage, the activation energy by lateral growth can be considered as a growth activation energy to some extent. In that point, microwave annealing reduced the growth activation energy.

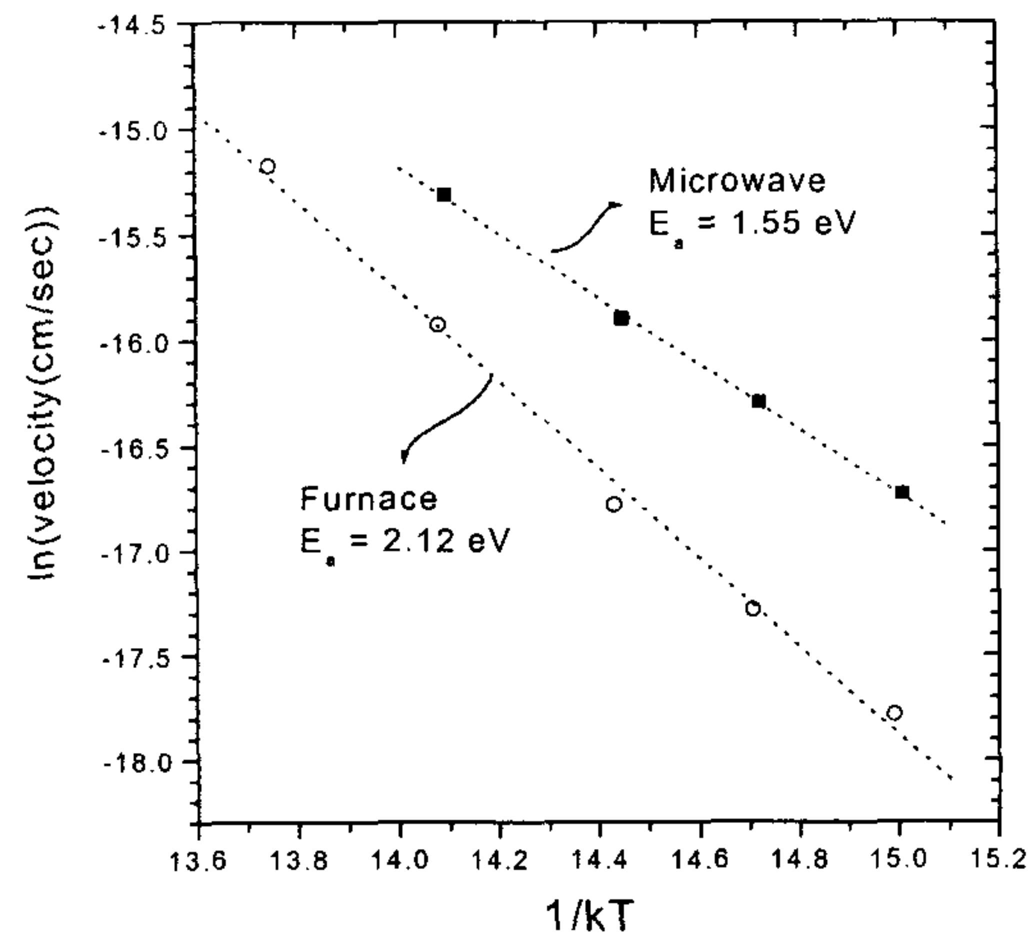

Figure 4. Arrehnius plot of the velocity of lateral crystallization at various temperatures.

The growth mechanisms of SMC and SMLC are $NiSi_2$-precipitates mediate process and the growth of c-Si grains are limited by the diffusion of Ni atoms thorough $NiSi_2$ precipitates [6]. Thus, it is believed that the microwave annealing not only supplies heat to Si substrate but also enhances the atomic mobilities in $NiSi_2$ precipitates and at $NiSi_2$/a-Si interface. The mobility enhancement may originate from interaction of microwave ac field and the mobile species, resulting in the additional supply of energy to the mobile species. The same phenomenon is related to the fast evolution of hydrogen in PECVD a-Si films during microwave annealing [4].

The enhancement of diffusion and reaction rate by microwave annealing [7,8] can be found in ceramic systems and the enhanced mass transport in NaCl single crystal is taken place through the increase of ionic current [9]. Theories such as non-thermal phonon distribution [10] and the ponderomotive force [11] have been proposed

Figure 5 shows the I-V characteristics of the intrinsic poly-Si TFTs. 100-nm thick a-Si films deposited by PECVD at 310 °C were crystallized by microwave annealing at 550 °C for 12 h. An 80-nm thick SiO_2 by LPCVD at 450 °C and a 300 nm thick poly-Si by LPCVD at 620 °C were employed as for gate dielectric and gate electrode, respectively. The

field effect mobility of the TFT by microwave annealing is 21.5 $cm^2/V{\cdot}s$, while that of the TFT with furnace annealing at 600 °C for 48 h is 20.0 $cm^2/V{\cdot}s$ and 5.6 V, respectively. The result shows that the forced crystallization at lower temperature does not degrade the cell performance.

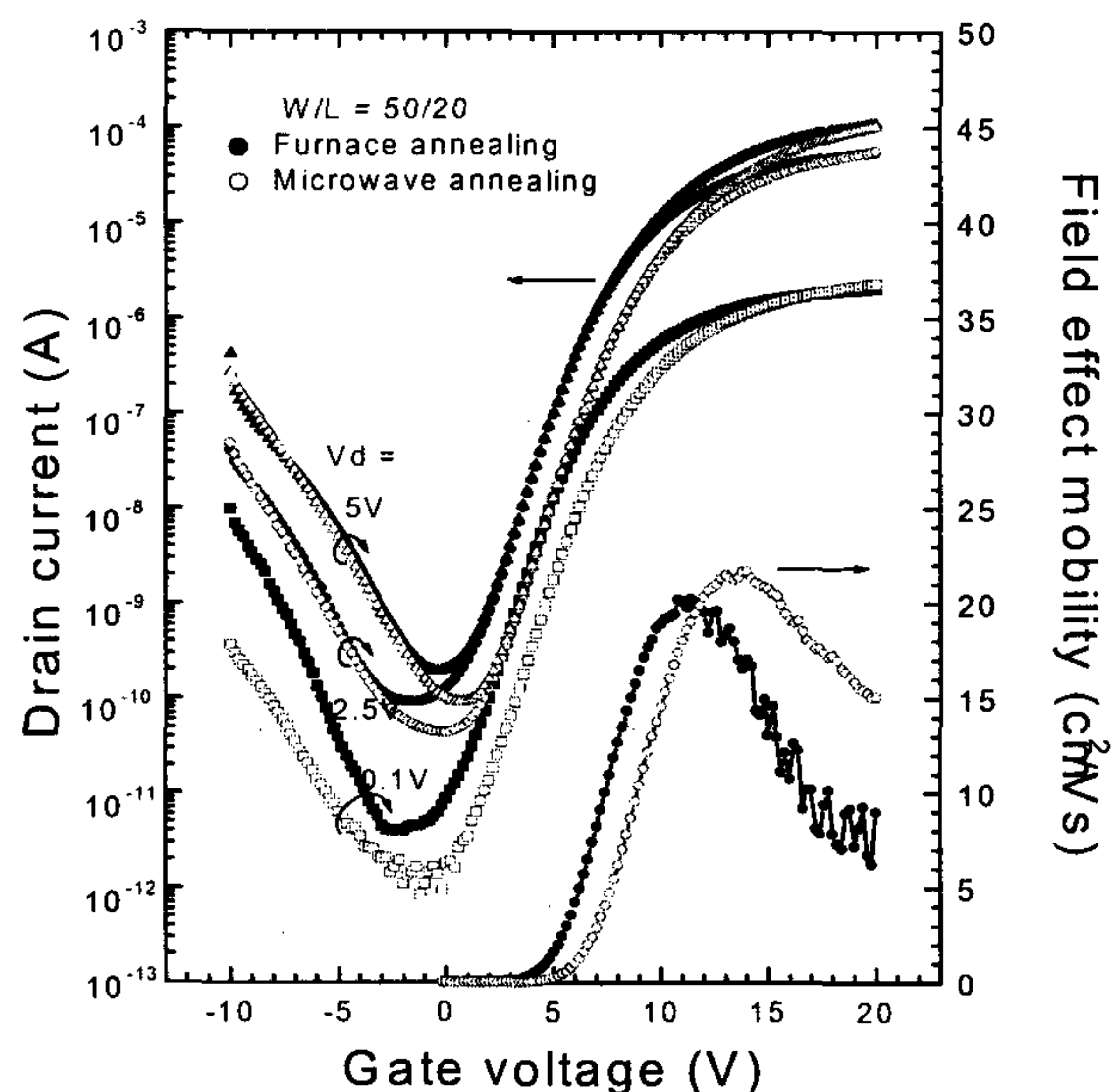

Figure 5. Characteristics of TFTs with intrinsic poly-Si films by microwave annealing and furnace annealing.

The TFT fabricated with Ni-SMC poly-Si films crystallized from Si_2H_6 a-Si films by microwave at 500 °C for 6 h showed 2.6 $cm^2/V{\cdot}s$, while that fabricated with Ni-SMLC by microwave at 500 °C for 6 h showed 21 $cm^2/V{\cdot}s$. The Ni-SMC process reduces the mobility due to metal contamination and the Ni-SMLC improved the mobility due to grain alignment along the channel length direction. The combination of microwave annealing of less amount of Ni coating is necessary to improve the mobility.

4. Conclusions

Microwave annealing lowered the crystallization temperature and shortened the annealing time. The combination of Ni and microwave applications on a-Si films further enhanced the crystallization. The enhancement was due to both reduced nucleation activation energy and growth activation energy. The mobility enhancement by microwave application may originate from interaction of microwave ac field and mobile species, resulting in the additional supply of energy to the mobile species. The combination of metal-induced crystallization and microwave-induced crystallization might be a useful technique to lower crystallization temperature further. The forced crystallization at lower temperature did not degrade TFT characteristics. The improvement of TFT characteristics is necessary.

References

[1] D. K. Sohn, S. C. Park, S. W. Kang, and B. T. Ahn, J. Electrochem. Soc. 144, 3592 (1997).

[2] J. H. Ahn, and B. T. Ahn, J. Electrochem. Soc. 148, H115 (2001).

[3] G. Liu and S. Fonash, Appl. Phy. Lett. 62, 2554 (1993)

[4] J. N. Lee, B. J. Lee, D. G. Moon and B. T. Ahn, Jpn. J. Appl. Phys. 36, 6862 (1997).

[5] J. H. Ahn, J. N. Lee, Y. C. Kim and B. T. Ahn, Current Applied Physics 2, 135 (2002)

[6] C. Hayzelden and J. L. Batstone, J. Appl. Phys. 73, 8279 (1993)

[7] M. A. Janney, H. D. Kimrey, M. A. Schmiat and J. O. Kiggan, J. Am. Ceram. Soc., 74, 1675 (1991)

[8] D. A. C. Stuerga and P. Gaillard, J. Microwave Power and Electromagnetic Energy 31, 87 (1996).

[9] S. Freeman, J. Booske, R. Cooper and B. Meng, Mat. Res. Symp. Proc. 347, 479 (1994).

[10] J. H. Booske, R. F. Cooper, and I. Dobson, J. Mater. Sci. 7, 495 (1992).

[11] K. I. Rybakov and V. E. Semenov, Phys. Rev. B 49, 64 (1994).