HOKKAIDO UNIVERSITY

Title	Direct Evidence of Polycrystalline Silicon Thin Films Formation during Aluminum Induced Crystallization by In-Situ Heating TEM Observation
Author(s)	Ii, Seiichiro; Hirota, Takeshi; Fujimoto, Kensuke; Sugimoto, Youhei; Takata, Naoki; Ikeda, Ken-ichi; Nakashima, Hideharu; Nakashima, Hiroshi
Citation	MATERIALS TRANSACTIONS, 49(4), 723-727 https://doi.org/10.2320/matertrans.MRA2007312
Issue Date	2008-04-01
Doc URL	http://hdl.handle.net/2115/75557
Type	article
File Information	Direct Evidence of Polycrystalline Silicon Thin Films Formation during Aluminum Induced Crystallization by In-Situ Heating TEM Observation.pdf

Instructions for use

Hokkaido University Collection of Scholarly and Academic Papers : HUSCAP

Materials Transactions, Vol. 49, No. 4 (2008) pp. 723 to 727
©2008 The Japan Institute of Metals

Direct Evidence of Polycrystalline Silicon Thin Films Formation during Aluminum Induced Crystallization by *In-Situ* Heating TEM Observation*[1]

Seiichiro Ii[1], Takeshi Hirota[2*2], Kensuke Fujimoto[2*3], Youhei Sugimoto[3*4], Naoki Takata[4], Ken-ichi Ikeda[5], Hideharu Nakashima[5] and Hiroshi Nakashima[6]

[1]*Department of Mechanical Engineering, Faculty of Engineering, Sojo University, Kumamoto 860-0082, Japan*
[2]*Department of Molecular and Materials Sciences, Interdisciplinary Graduate School of Engineering Sciences, Kyushu University, Kasuga 816-8580, Japan*
[3]*Department of Applied Science for Electronics and Materials, Interdisciplinary Graduate School of Engineering Sciences, Kyushu University, Kasuga 816-8580, Japan*
[4]*Department of Metallurgy and Ceramics Science, Graduate School of Science and Technology, Tokyo Institute of Technology, Tokyo 152-8552, Japan*
[5]*Department of Electrical and Material Sciences, Faculty of Engineering Sciences, Kyushu University, Kasuga 816-8580, Japan*
[6]*Art, Science and Technology Center for Cooperative Research, Kyushu University, Kasuga 816-8580, Japan*

The formation behavior of polycrystalline silicon thin films during the aluminum induced crystallization (AIC) process was investigated by scanning transmission electron microscopy (STEM) and *in-situ* heating transmission electron microscopy (TEM) observations. The STEM observation and electron dispersive X-ray spectroscopy (EDS) analysis of *ex-situ* heat-treated specimen revealed that the a-Si layer and Al layer switched the positions with each other during the heat treatment, resulting the crystallization of the a-Si layer. Furthermore, the *in-situ* heating TEM observation and EDS analysis of as-deposited specimen revealed the mixed state of Si and Al in an a-Si/Al film and the lateral growth of crystalline Si grain during the heating. The mechanism of AIC and switching layers were also discussed from the experimental results and the binary phase diagram of Al-Si system. [doi:10.2320/matertrans.MRA2007312]

(Received December 17, 2007; Accepted January 21, 2008; Published March 5, 2008)

Keywords: *aluminum induced crystallization, polycrystalline silicon thin film, transmission electron microscopy, in-situ heating observation, metastable state*

1. Introduction

Si thin films on glass substrate are widely applied to a variety of electronic devices. Recently, low-temperature polycrystalline silicon (poly-Si) films on inexpensive substrates (non-alkali glass) are expected to be applied in practice owing to requirement for the good device performance and low fabrication cost. The materials are generally fabricated at low temperatures below 873 K. The solid-phase crystallization (SPC) process is one of conventional way for the poly-Si film fabrication by the crystallization of amorphous Si (a-Si) film. However, this process has a trade-off relationship between crystallization temperature and time at temperatures below 873 K.[1] Therefore, for achieving the fabrication of poly-Si film on glass substrate at lower temperature, laser annealing crystallization (LAC) and metal induced crystallization (MIC) have been intensively studied as promising candidates to replace the standard SPC.[2,3]

Al-induced crystallization (AIC) is one of MIC processes using a metal/a-Si bilayer structure, which can induce the crystallization of a-Si for a rather short time of 5.4 ks even at a low temperature of 773 K.[4,5] It has been reported that AIC process is effective for decreasing the activation energy of the a-Si crystallization due to the Al layer playing an important role of the catalyst for a-Si crystallization.[6] The basic process of the AIC process consists of the heating a-Si/Al/substrate to lower temperature than 850 K, which is a eutectic temperature on the Al-Si binary alloy. During this process, Nast *et al.* have observed an interesting phenomenon of switching each position of the a-Si/Al bilayer on the glass substrate, resulting in the direct fabrication of poly-Si film on the substrate.[4] Nast and Hartmann have pointed out that native Al oxide inserted into the a-Si/Al interface plays an essential role in the final crystal quality of poly-Si film.[5] The AIC process with a native Al oxide layer, *i.e.*, the deposition of an a-Si/Al bilayer with breaking the vacuum, is recently focused on several studies of performing the AIC under various conditions in order to prepare the poly-Si having a large grain size at a low temperature.[4–11] On the other hand, Kim *et al.* have reported that a-Si/Al bilayer deposited under vacuum condition switched positions with each other and the switching rate is higher than that of a-Si/Al bilayer including the oxide film on the top of layers.[7] Sugimoto *et al.* have investigated that the effect of heat-treating temperature and film thickness ratio on the quality of poly-Si by crystal orientation analysis using electron back scattering diffraction and transmission electron microscopy (TEM).[12] Moreover, Schneider *et al.* have focused that the nucleation of Si in the Al_2O_3/a-Si/Al layers during cooling process after heat-treatment and have reported that the controlling of the nucleation of Si was closely related to the controlling of the growth of Si during the heating process. However, there are no observations of the crystallization process of a-Si in a-Si/Al bilayer.[13,14]

[*1] This paper is Originally Published in Japanese in J. of Japan Institute of Metals **71** (2007) 158–163.

[*2] Graduate Student, Kyushu University. Present address: Mitsubishi Heavy Industries, Ltd., Japan

[*3] Graduate Student, Kyushu University

[*4] Graduate Student, Kyushu University. Present address: Seiko Epson Corp., Japan

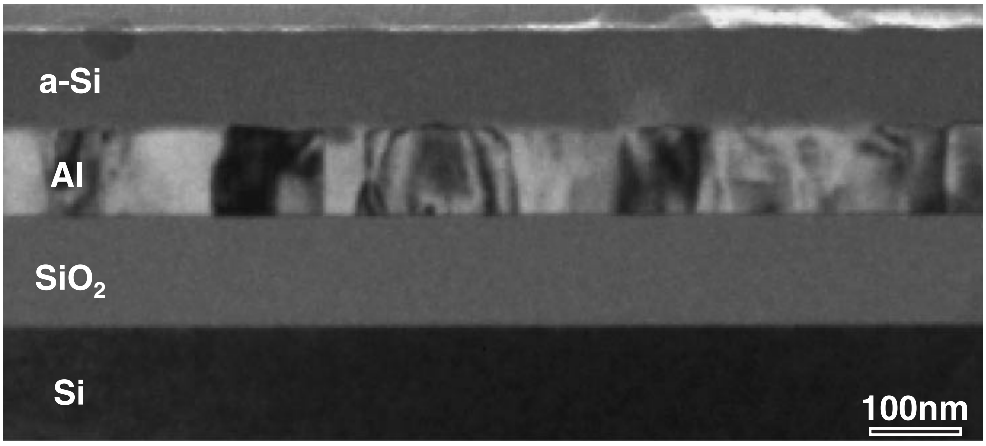

Fig. 1 Cross-sectional BF-TEM image of as-deposited a-Si/Al film.

The purpose of our study is to investigate the microstructural change of a-Si/Al bilayer during heating by using *in-situ* TEM technique, Scanning TEM (STEM) and energy dispersed X-ray spectroscopy (EDS) systematically. We also discussed crystallizing mechanism from the obtained results.

2. Experimental Procedure

SiO_2 was thermally grown onto single crystal Si substrate by dry oxidation at 1273 K to form the SiO_2/Si substrate. The thickness of the SiO_2 layer was approximately 130 nm. Both Al and a-Si films were deposited on the SiO_2/Si substrate by electron beam deposition without breaking the vacuum atmosphere, where both thickness of Al and a-Si layer were 100 nm. The obtained wafer was annealed at 673 K for 36 ks in a dry nitrogen atmosphere. The specimen for TEM and STEM observation were prepared by standard microsampling technique using HITACHI FB-2000 focused Ga^+ ion beam apparatus.

The microstructure and elemental analysis of the Al/a-Si bilayer was performed by TECNAI 20F electron microscope equipped with field emission type electron gun and STEM high angle annular dark field (HAADF) image detector. The elemental analysis was measured by energy dispersive X-ray spectroscopy (EDS). *In-situ* heating TEM observations were also performed by FEI TECNAI 20 and GATAN model 652 double tilt specimen heating holder. The specimens were heated up to 473, 553 and 623 K in the electron microscope. The microstructral change during heating and keeping at those temperatures is recorded by VTR with a flame rate of $30\,s^{-1}$. In addition, the specimen annealed at 473 K was kept for 0.3 ks in the microscope, and then each layer was identified by micro area electron diffraction patterns and composition analysis by using EDS measurements. Both electron microscopes were operated at the accelerating voltage of 200 kV.

3. Results and Discussion

Figure 1 shows a bright field image of the a-Si/Al film as deposited. The observed wafer consists of the SiO_2, Al and a-Si on the substrate of Si wafer. We confirmed that the Si substrate of single crystal, amorphous SiO_2 and polycrystalline Al by selected area electron diffraction patterns. Figure 2(a) shows the STEM-HAADF image of the wafer heated at 673 K for 36 ks. And Figs. 2(b) to (d) show elemental maps obtained by EDS measurements. Figure 2 shows that the Al and a-Si are completely change their positions each other. Sugimoto *et al.* have reported that the thickness of the crystallized poly-Si layer was closely related to an initial thickness of the Al layer from the cross-sectional microstructure observations of the wafer, and they have concluded that the initial thickness ratio of Al and a-Si layers was 1:1 for the formation of the high quality polycrystalline Si film.[11] Therefore, it can be considered that the Si layer shown in Fig. 2 is a part of poly-Si.

In order to observe the microstructural change during heating in direct, we performed the *in-situ* TEM observation. Figure 3 shows representative images showing of microstructural change of as deposited a-Si/Al bilayer during *in-situ* heating TEM observation. The temperature is reached up to 533 K. A time interval from Figure 3(a) to (f) is approximately 15 s, respectively. In these figures, the black contrast can be observed in the vicinity of the interface between Al and a-Si and grows in the a-Si layer. In addition, we confirmed that the further heating enhances the growth of the black contrast to the lateral direction in the initial a-Si layer.

Figure 4(a) and (b) show bright field images of the specimen before (a) and after (b) *in-situ* heating at 473 k for 0.3 ks in TEM, respectively. It should be noted that the two images were taken from the same region in the specimen. The switching their position of two a-Si and Al layers is starting in the wafer, and the microstructural change was confirmed in the a-Si layer. In addition, it was also observed that the microstructure of the Al layer changed during the *in-situ* heating.

In order to investigate the microstructure of the films after the *in-situ* heating in detail, we identified the layer by the selected area electron diffraction pattern and STEM-EDS measurement. Figure 5 shows a bright field image (a) in the wafer *in-situ* heated at 473 K for 0.3 ks and selected are electron diffraction patterns ((b) to (e)) take from the region B to E shown in Fig. 5(a), respectively. Several reflection

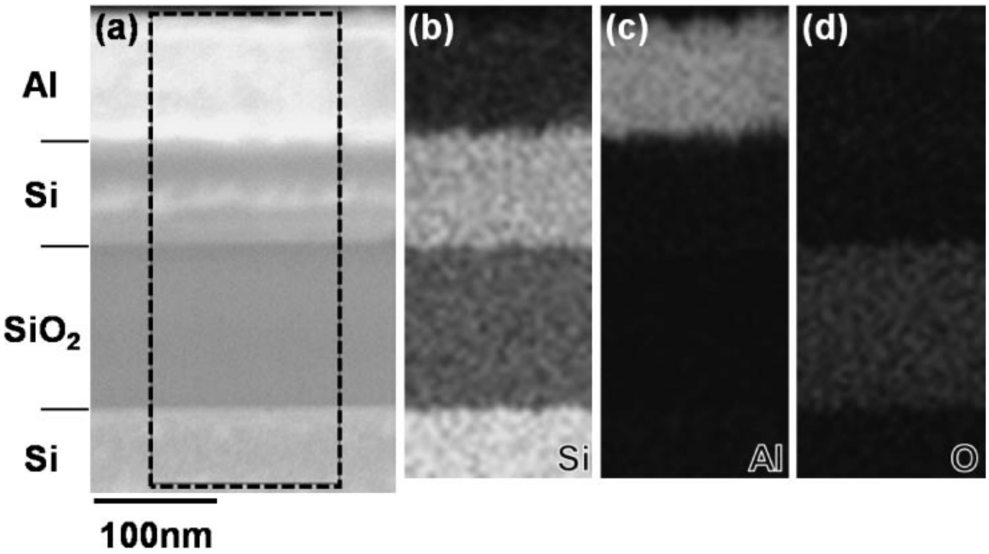

Fig. 2 (a) Cross-sectional HAADF-STEM images of a-Si/Al annealed at 673 K for 36 ks and elemental maps of (b) Si, (c) Al and (d) O of square region in (a).

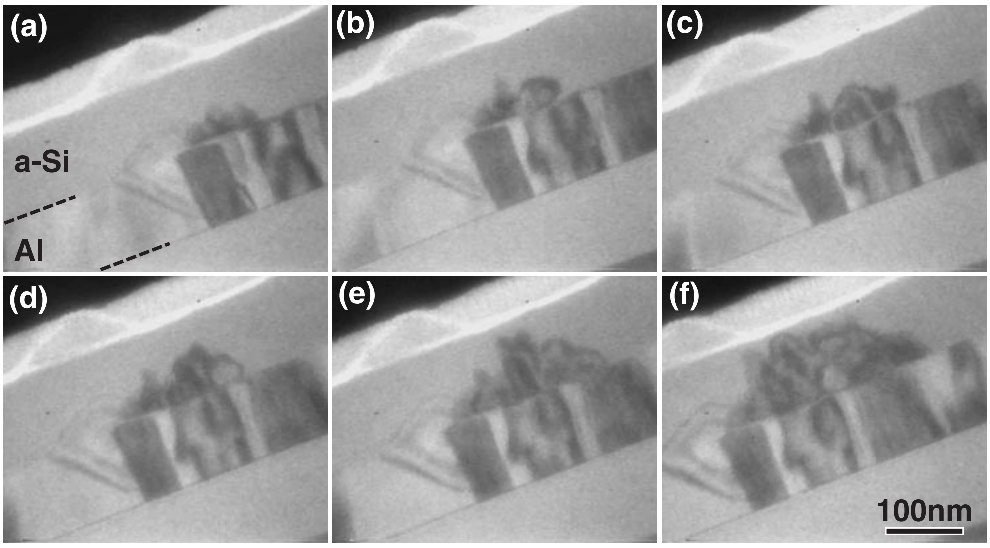

Fig. 3 A series of BF-TEM images of a-Si/Al film taken during *in-situ* heating at 553 K (average time interval 15 s).

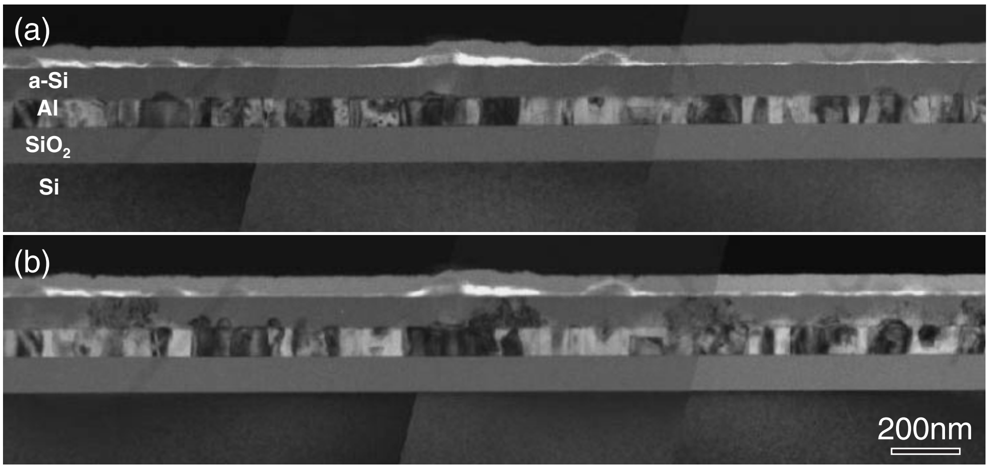

Fig. 4 BF-TEM images of a-Si/Al film. (a) as-deposited and (b) *in-situ* heated at 473 K for 0.3 ks.

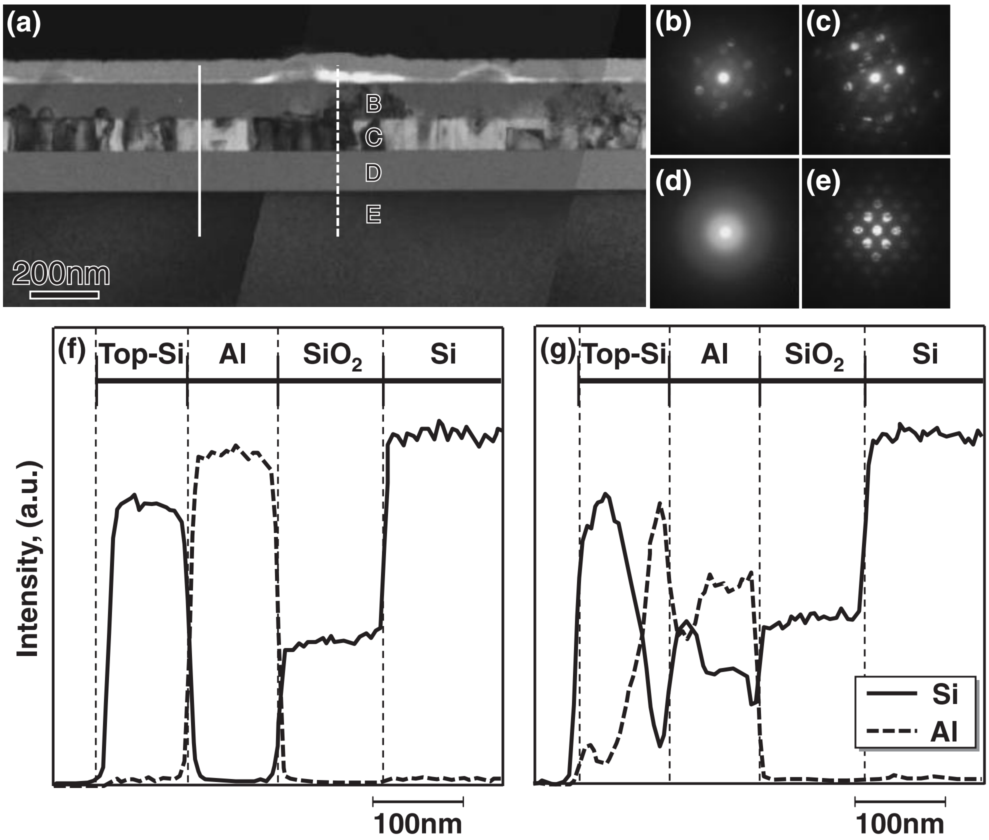

Fig. 5 (a) BF-TEM image, (b) to (e) micro diffraction patterns and (f) and (g) EDS line analysis profile of *in-situ* heated (at 473 K for 0.3 ks) a-Si/Al film.

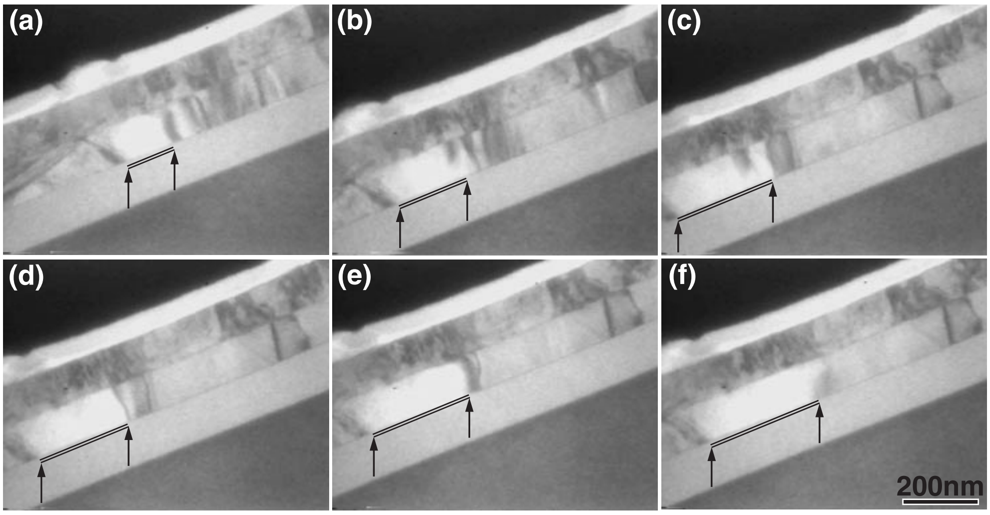

Fig. 6 A series of BF-TEM images of a-Si/Al film taken during *in-situ* heating at 623 K (average time interval 15 s).

spots obtained from the initial a-Si layer as shown in Fig. 5(b) clearly indicates that the crystallization partially occurs in the a-Si layer during the heating. In addition, we measured the chemical composition of each layers by STEM-EDS measurements. Figure 5(f) shows a composition profiles of Si and Al measured along white solid line shown in Fig. 5(a). From the Fig. 5(f), we can confirm that the each layer consists of Si and Al, respectively. On the other hand, the line profiles of other area shown by white broken line in Fig. 5(a), indicate that Si and Al are solved to each other and are mixed state in the Si and Al layers. These results suggest that the Si and Al layer forms each solid-solution through the interdiffusion at the initial stage of heating, and then Si is crystallized and forms polycrystalline.

Figure 6 shows representative bright field images of the same specimen shown in Fig. 3 during further heating in TEM up to 623 K. Average time interval shown in Figs. 6(a) to (f) is also 15 s, respectively. The white contrast shown by

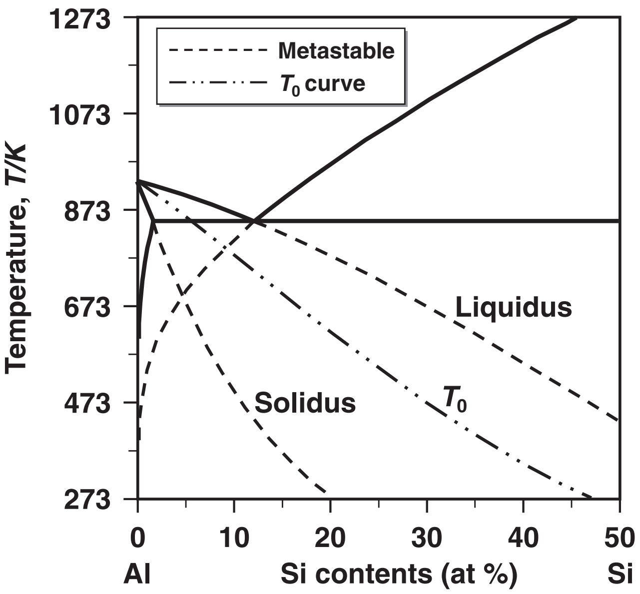

Fig. 7 The Al-Si phase diagram with the metastable line and the T_0 curve.

double black lines and single black arrows is grown to the lateral direction in the Al film. Obtained results of the elemental analysis show that the white contrast in the Al layer corresponds to the crystalline Si. Further annealing, we confirmed that the crystalline Si grew to the lateral direction in the polycrystalline Al layer.

From the obtained results, we considered that the a-Si are crystallized to poly-Si after forming the solid-solution of Al and Si in the initial a-Si and Al layer at early stage of the heating. In addition, crystalline Si grew to the lateral direction in the Al layer with further heating. In contrast, the Al-Si binary equilibrium phase diagram shown by solid line in Fig. 7[15)] represents that Si cannot solve in Al between the temperature between 473 K and 623 K, which is performed *in-situ* heating TEM observation. We considered that the specimen investigated in this study is non-equilibrium state, since the film is consisting of amorphous Si and thin Al layer on the wafer. A broken line extended from the equilibrium liquidus and solidus line shown in Fig. 7 is the metastable line of Al in Al-Si binary system. In the region between broken liquidus and solidus line, Si can be solved into Al even at low temperature region. Especially, the initial Si layer on the substrates exhibits amorphous phase in our studied specimen. Furthermore, both a-Si and Al layers have extremely thin, whose thickness of about 100 nm. These conditions are quite different from that of bulk crystalline materials, that is, equilibrium state, following the equilibrium phase diagram. Therefore, Si can be solved into the Al between the 473 and 553 K as shown in Fig. 7, although this is the non-equilibriums state. That is the reason why the solid solution can be formed during the *in-situ* heating. Additionally, taking into account metastable line of Si as the same of Al as mentioned above, Si is also solved into the initial Al layer. However, the specimen is reached to the equilibrium state by further heating, Al and Si cannot solved to each other, the mixed Al and Si separates into each crystalline phase showing a characteristic morphology of dendritic phase.[11)]

The obtained results suggests that the deposited a-Si and Al is formed each solid solution because of their non-equilibrium state, and the transition to the equilibrium state grows the crystalline Si. This phenomenon is considered with the same as multilayer consisted of the a-Si and Al reported by Konno *et al.*[16)] Further study about the nucleation site of crystallization is required for understanding the switching their positions of Si and Al layers in detail.

4. Concluding Remarks

We investigated the microstructural change of a-Si/Al film deposited onto the thermally oxidized Si substrate by using *in-situ* heating TEM observation and STEM-EDS measurements. The obtained results are shown as follows:

(1) STEM-EDS analysis revealed that the Al and a-Si layers have switched their positions with each other during the heating at 673 K for 36 ks in the AIC process.

(2) *In-situ* heating TEM observation directly revealed the solid solution of Al in Si and Si in Al and crystallization of Si during annealing at 473 K. And the crystalline Si grew to the lateral direction in the Al layer with further annealing.

(3) Since the a-Si and Al layers in the wafer used in this study is non-equilibrium state, respectively, Si and Al is formed solid-solution to each other in the layers. However, further annealing brings to the equilibrium, therefore Al and Si is separated to two layers.

Acknowledgements

A part of the study is financially supported by Grant-in-Aid for Scientific Research, Ministry of Education, Culture, Sports, Science and Technology, Japan.

REFERENCES

1) A. T. Voutsas: Appl. Surf. Sci. **208–209** (2003) 250–262.
2) A. Hara, K. Yoshino, F. Takeuchi and N. Sasaki: Jpn. J. Appl. Phys. **42** (2003) 23–27.
3) Z. Jin, G. A. Bhat, M. Yeung, H. S. Kwok and M. Wong: J. Appl. Phys. **84** (1998) 194–200.
4) O. Nast, T. Puzzer, L. M. Koschier, A. B. Sproul and S. R. Wenham: Appl. Phys. Lett. **73** (1998) 3214–3216.
5) S. Gall, M. Muske, I. Sieber, O. Nast and W. Fuhs: J. Non-Cryst. Solids **299–302** (2002) 741–745.
6) M. Doi, F. Katsuki, H. Kumagai and M. Takagi: J. JILM. **57** (2007) 30–36. (in Japanese)
7) H. Kim, D. Kim, G. Lee, D. Kim and S. H. Lee: Sol. Energy Mater. Sol. Cells **74** (2002) 323–329.
8) O. Nast and A. J. Hartmann: J. Appl. Phys. **88** (2000) 716–724.
9) I. Sieber, R. Schneider, I. Doerfel, P. Schubert-Bischoff, S. Gall and W. Fuhs: Thin Solid Films **427** (2003) 298–302.
10) O. Nast and S. R. Wenham: J. Appl. Phys. **88** (2000) 124–132.
11) P. I. Widenborg and A. G. Aberle: J. Cryst. Growth **242** (2002) 270–282.
12) Y. Sugimoto, N. Takata, T. Hirota, K. Ikeda, F. Yoshida, H. Nakashima and H. Nakashima: Jpn. J. Appl. Phys. **44** (2005) 4770–4775.
13) J. Schneider, A. Schneider, A. Sarikov, J. Klein, M. Muske, S. Gall and W. Fuhs: J. Non-Cryst. Solids **352** (2006) 972–975.
14) A. Sarikov, J. Schneider, M. Muske, S. Gall and W. Fuhs: J. Non-Cryst. Solids **352** (2006) 980–983.
15) T. B. Massalski: *Binary Alloy Phase Diagrams Vol. 1*, (American Society for Metals) pp. 164–165.
16) T. J. Konno and R. Sinclair: Philos. Mag. B **66** (1992) 749–765.