Observation of Magnesium-Induced Crystallization (Mg-MIC) of a-Si Thin Film

Takashi Ikehata1*, Ryota Sasajima1, Motomu Saijo1, Naoyuki Sato1 and Haruhiko Udono1

1Graduate School of Science and Engineering, Ibaraki University, Hitachi, Ibaraki 316-8511, Japan

E-mail: takashi.ikehata.eng@vc.ibaraki.ac.jp

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Magnesium induced crystallization (Mg-MIC), that is, the low temperature crystallization process of an amorphous silicon (a-Si) film activated by magnesium has first been investigated. The crystallization temperature is evaluated as low as 450 °C from Raman spectroscopy in contrast to 600 °C-800 °C in the solid phase crystallization (SPC) process (only a-Si film is heated). The crystallization is found to occur via the formation of intermediate phase: the silicide (Mg5Si3) as reported in the Ni-MIC studies. A filamentary structure expected from the previous studies is not observed.

1. Introduction

The Magnesium silicide (Mg5Si3) is an indirect, narrow-band-gap semiconductor composed of nontoxic and resource-abundant elements; it has been expected for a base material of thermoelectric and infrared devices [1-3]. The authors have been devoted to prepare a poly-crystalline Mg5Si thin film by annealing a sputter-deposited amorphous Mg/Si bilayer in argon gas atmosphere. In this study, the growth of poly-crystalline Mg5Si was identified in the temperature range from 300 °C to 400 °C [4]. Recently, the authors observed that the Raman peak at 253 cm⁻¹ typical of Mg5Si [3] disappeared and the peak at 520 cm⁻¹ typical of poly-Si [5] newly appeared at the temperature higher than 450 °C. This result was considered to suggest the magnesium-induced crystallization, Mg-MIC. In the MIC process, a eutectic or silicide-forming metal element promotes crystallization of a-Si at relatively low temperature. The MIC process has been explored for a half century as a process to prepare poly-Si thin films economically for applications to large-area solar cells and TFTs of flat display panels [6-15]. So far, 20 different elements have been explored and confirmed to have the MIC effect [10]. However, as long as the authors know, there is no report on Mg-MIC. In the present study, crystallization of an a-Si film by the Mg-MIC mechanism is discussed.

2. Brief Review of Metal Induced Crystallization (MIC)

The MIC study has a long history by many researchers [6-15]. This technology has been expected as an economical method of preparing a poly-Si film from an a-Si film deposited by CVD or sputtering. Knaepen et al. [10] investigated the crystallization temperature of 20 metal elements that are eutectic or silicide-forming. The results are summarized in Table 1. The crystallization temperature by SPC is 790 °C, while the lowest crystallization temperature is 200 °C by Au-MIC. The temperature of 450 °C by Mg-MIC is from the present study. The microstructure and the crystallinity of synthesized poly-Si films have actively been investigated by Raman spectroscopy, XRD and the TEM analysis. Recently the film was applied to a PV cell and yielded a maximum conversion efficiency of 6% [15]. The mechanism of MIC has ever been discussed by Nast and Hartmann [11] for eutectic elements and by Hayzelden and Batstone [12], Jin et al. [13] and
Knaepen et al. [10] for silicide-forming elements. They claimed that the change of Si from amorphous phase to crystalline phase occurs via the intermediate phase, that is silicide for silicide-forming elements and alloy for eutectic elements. Such a phase change is driven by the difference in thermodynamic energy among three phases. The Ni-MIC mechanism according to Knaepen et al. is shown schematically in Fig. 1 First Ni is deposited on an a-Si layer at low temperature (a). At elevated temperature, a NiSi$_2$ layer is formed through co-diffusion of Ni and Si (b). If temperature is further elevated, the poly-NiSi$_2$ layer breaks at the a-Si interface and makes nodules (c). These NiSi$_2$ nodules move into a-Si driven by Ni diffusion leaving poly-Si whiskers or filaments. The filamentary structure in the synthesized poly-Si layer has been demonstrated from HRTEM measurements [15]. The filamentary structure is of interest in the present Mg-MIC study as well.

| Element | Interaction | T [°C] |
|---------|-------------|--------|
| Au      |             | 200    |
| Al      | Eutectic    | 260    |
| Ag      |             | 530    |
| Cu      |             | 430    |
| Mg      |             | 450    |
| Pd      |             | 540    |
| Ni      |             | 590    |
| Pt      |             | 630    |
| Mn      |             | 700    |
| Rh      |             | 710    |
| Co      |             | 730    |
| Fe      |             | 730    |
| Cr      |             | 740    |
| Ti      | Silicide-forming | 740 |
| Nb      |             | 740    |
| Ir      |             | 740    |
| Ta      |             | 740    |
| Re      |             | 740    |
| Mo      |             | 740    |
| V       |             | 740    |
| Hf      |             | 750    |
| Ru      |             | 750    |
| Zr      |             | 770    |
| W       |             | 770    |
| a-Si    | SPC         | 790    |
3. Experimental Results and Discussion

3.1 Annealing temperature dependence

Figure 2 shows a schematic representation of the sample preparation. An a-Si layer (310 nm) and then a Mg layer (720 nm) were deposited on a single-crystal sapphire substrate (10 x 10 x 0.5 mm, r plane) at room temperature by using independent rf sputtering sources. The substrate has been ultrasonically cleaned in acetone for 15 minutes and heated in vacuum at 300 °C for 15 minutes prior to the deposition. Mg and Si targets have the same size of φ25.4 mm x 3 mm and the purity of 99.95% and 99.999%, respectively. The thickness of each layer is chosen to prepare a stoichiometric Mg$_2$Si film with a thickness of 1 µm. This Mg/Si bilayer sample is put on a heater (1 inch diameter) and annealed for two hours following a ramping period of 20 minutes in argon gas.
of 900 Pa. The annealed sample is taken out of the chamber after the temperature decreases down to 100 °C by natural cooling. The property of the sample was analyzed by using Raman spectroscopy, XRD and SEM-EDS.

Figure 3 shows Raman spectra of three samples: an as-deposited Si film (310 nm in thickness) (bottom), a post-annealed (473 °C, 2 hours in Ar of 900 Pa) Si film (middle) and a c-Si (111) wafer for reference (top). The SN xxx appearing in the text and in the figures hereafter denotes the sample number connected to each preparation condition. The spectra of film samples were measured at five locations (four corners and one center) on each sample and were superposed in the figure. The spectrum of the as-deposited Si layer shows no apparent peak except broad and obscure peak near 480 cm⁻¹. It suggests that the sample is amorphous [16]. The other sample that is sputter-deposited and then annealed at 473 °C for 2 hours appears still amorphous because the spectrum is very similar to the as-deposited sample. Therefore, it is concluded that a-Si alone does not change into crystal structure at temperature as low as 473 °C.

Figure 4 shows Raman spectra of Mg (720 nm)/Si (310 nm) bilayers annealed at 214 °C (bottom), 355 °C (lower-middle) and 453 °C (upper-middle) for 2 hours in Ar of 900 Pa, together with a Mg₂Si bulk crystal for reference (top). No apparent peak is observed at 214 °C, suggesting no crystallization happens at this temperature. At 355 °C, on the other hand, a sharp peak corresponding to the TO/LO mode of Mg₂Si crystal appears at 253 cm⁻¹ [3] and therefore, demonstrates the solid-phase synthesis of poly-Mg₂Si. However, this peak disappears when the annealing temperature is elevated up to 453 °C; instead, another peak appears at ~520 cm⁻¹ that is typical of the TO/LO mode of Si crystal. Therefore, it may be concluded that the lower-middle and upper-middle spectra in Fig. 4 prove the presence of Mg-MIC.

Raman peak intensities at 253 cm⁻¹ and 520 cm⁻¹ are plotted as a function of annealing temperature as shown in Fig. 5. The growth of poly-Mg₂Si starts at 300 °C and takes a maximum at 375-400 °C. However, the phase changes to poly-Si at 450 °C and higher. Therefore, it is found that Mg-MIC starts at about 450 °C.

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**Fig. 3.** Raman spectra of as-deposited and annealed a-Si layers (310 nm).

**Fig. 4.** Raman spectra of Mg/Si bilayer samples annealed at 214, 355 and 453 °C.
One question is the distribution and the condition of Mg atoms after the MIC process is completed: Are they evaporated? Or do they still remain in the sample? In Al-MIC, the positional exchange between Al and Si layers has commonly been observed in the silicon crystallization process, while in Ni-MIC, long and narrow polycrystalline silicon (poly-Si) whiskers with a NiSi$_2$ grain on each tip have been observed to grow in the a-Si layer. This difference may be attributable to the fact that Al is a eutectic element while Ni is a silicide-forming element. Since Mg is a silicide-forming element too, a filamentary poly-Si structure involving Mg grains is expected in the Mg/Si bilayer sample annealed at high-temperature.

We performed the SEM-EDS analysis to investigate the elemental distribution in the samples. Figure 6 (a) shows the EDS spectrum derived from the 30 µm x 40 µm area of the lower-annealing-temperature sample (350 °C, 2 hours) showing poly-Mg$_2$Si from the Raman spectroscopy. The Mg to Si ratio is 1.98 : 1 close to the stoichiometric ratio of 2 : 1. In the higher-annealing-temperature sample (483 °C, 2 hours) showing poly-Si, on the other hand, the Mg to Si ratio is 0.02 : 1 suggesting considerable evaporation of Mg at the elevated temperature.

![Fig. 5. Raman intensities at wavenumbers of 253 cm$^{-1}$ and 520 cm$^{-1}$ as a function of the annealing temperature.](image)

![Fig. 6. SEM-EDS spectra of Mg/Si bilayer samples annealed at (a) 350 °C for 2 hours (SN194) and (b) 483 °C for 2 hours (SN438).](image)
The surface and cross-sectional distributions of Si, Mg, O and Al derived from EDS (5 keV in the electron beam energy) of the latter sample (SN438) are given in Fig. 7. We can see a columnar structure of the film from the cross-sectional SEM image (Fig. 7 (f)). It is to be noted that the SEM image of Fig. 7 (f) is a little deformed laterally due to the static charging. The thickness of the film is estimated to be 1 µm in agreement with the design. In the film, only Si appears uniformly (Fig. 7 (g)), while Mg is not identified (Fig. 7 (h)). MgO grains with sub-micron size and irregular shape are identified on top of the film (Fig. 7 (c),(d)). These results may suggest that Mg atoms serving to crystallize a-Si by the MIC mechanism migrate on the top boundary of the film; then, the most part of them evaporate and the rest condense into Mg grains. Mg grains can be oxidized easily by putting the sample in air. The filamentary structure seen in the Ni-MIC studies is not identified in the present study from the SEM observation. The HRTEM analysis may be required to make it clearer.

### 3.2 Mg evaporation during sample annealing

In the preceding section, we mentioned a possibility of Mg evaporation during sample annealing. We evaluated the quantity of evaporated Mg atoms by using the setup shown in Fig. 8. A Mg layer of 5 µm in thickness was sputter-deposited on a c-Si (111) substrate. This test sample was put on the heater and heated at a given temperature for three hours in Ar gas of 900 Pa as in the Mg-MIC experiment. At 10 mm above the test sample, a QCM sensor to measure the deposition rate and the thickness of the Mg layer is installed. The example of data for 350 °C is shown in Fig. 9 (a). The evaporation occurs mainly in relatively early times (from 10 minutes to 20 minutes from the start of heating) and stops before 100 minutes. The thickness of deposited Mg layer as a function of temperature is given in Fig. 9 (b). It may be said that Mg evaporation is not significant at temperature lower than 400 °C, as expected from the synthesis of Mg2Si. On the other hand, the evaporation is considerable at 500 °C such that the amount of the evaporated magnesium is comparable with the initial amount in the test sample. These observations may be consistent with SEM-EDS results discussed above.
3.3 Annealing period dependence

The annealing period is changed from 0 to 2 hours (except the ramping period of 20 minutes) while the temperature is fixed at 500 °C as illustrated in Fig. 10. Raman spectra of annealed samples were obtained as described in the preceding section. Raman peak intensities at 253 cm\(^{-1}\) and 520 cm\(^{-1}\) are plotted as a function of annealing period in Fig. 11. The magnesium silicide is synthesized only for the period of 0 h. However it changes to poly-Si when the period is longer than 0.5 h. Fig. 12 shows atomic composition of Mg and Si analyzed on the same set of samples by SEM-EDS as a function of annealing period. Both Mg and Si are detected only in the sample for the annealing period of 0 h. In samples for the annealing period longer than 0.5 h, Mg is little detected. Therefore, results of Figs. 11 and 12 are consistent to each other. The reason why Mg\(_2\)Si is synthesized when the annealing period is 0 h may be that the sample experience the temperature higher than 450 °C (MIC temperature) for very short period while it does the temperature from 300 to 400 °C (suitable for Mg\(_2\)Si synthesis) for longer than 20 minutes. Therefore, it may conclude that the synthesis of Mg\(_2\)Si and the MIC phase change into Si occur rapidly within a couple of ten minutes.

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**Fig. 8.** Mg evaporation measurement using QCM. A 5 μm-thick Mg layer sputter-deposited on a Si (111) substrate is heated in Ar gas of 900 Pa for 3 hours.

**Fig. 9.** (a) An example of QCM signals: The deposition rate and the thickness as a function of time at annealing temperature of 350 °C. (b) The thickness of deposited Mg layer as a function of annealing temperature.
Fig. 10. Sequence diagram of the sample preparation for investigating annealing period dependence: Sputter deposited Mg/Si bilayer on a sapphire substrate was annealed at 500 °C in Ar gas of 900 Pa for 0, 0.5, 1.0 and 2.0 hours.

Fig. 11. Raman peak intensities of MgSi (253 cm\(^{-1}\)) and poly-Si (520 cm\(^{-1}\)) as a function of annealing period.

Fig. 12 Atomic composition of Mg and Si in the same set of samples as shown in Fig. 11 as a function of annealing period.

5. Summary

The magnesium-induced crystallization (Mg-MIC) of a sputter-deposited amorphous silicon film was explored. Conclusions are summarized as follows:

(1) Low-temperature (450 °C) crystallization of a-Si layer on a sapphire substrate was achieved by depositing Mg and annealing the resulting Mg/Si bilayer in Ar gas of 900 Pa for longer than 0.5 hour.

(2) The a-Si layer alone (SPC) did not crystalize even at 500 °C.

(3) Crystallization took place rapidly (a few tens of minutes) via the formation of MgSi as the intermediate phase.

(4) From the above observations, Mg-MIC was confirmed as the crystallization mechanism.

(5) The filamentary structure reported in the previous Ni-MIC studies was not identified from the SEM observation. The HRTEM observation will be an option to investigate it.
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