Solid-Phase Synthesis of Mg2Si Thin Film on Sapphire Substrate

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Magnesium silicide (Mg2Si) is expected as a semiconductor material for thermoelectric devices though synthesis of the thin film has been difficult due to difference in thermodynamic properties of Mg and Si. The authors have succeeded in preparing a poly-crystalline Mg2Si thin film with a thickness of ~1μm and strong (111) orientation on a sapphire substrate (r plane). The method includes sputter deposition of a Mg/Si bilayer from independent Mg and Si sources and post-annealing (2 h) in argon gas at 900 Pa. The optimum annealing temperature for the Mg2Si film synthesis is found to be 300-400°C.

1. Introduction
Magnesium silicide is a narrow-band-gap semiconductor consisting of non-toxic, resource-abundant elements, Mg and Si. It has recently been expected as a key material for realizing the thermoelectric power generation from waste heat and for the advanced infrared technology. However, large difference in thermodynamic properties of Mg and Si has made the synthesis of a stoichiometric Mg2Si film by physical vapor deposition (PVD) rather challenging [1]. Nevertheless, many studies have been devoted to make high-quality Mg2Si films by using various deposition methods such as MBE [1,2], sputter deposition [3-7], and vacuum evaporation [8]. In these studies, single-crystal silicon has commonly been used as the substrate because only Mg is needed to be deposited to synthesize Mg2Si. A substrate which does not include Si, on the other hand, needs the deposition of both Mg and Si to yield Mg2Si. Therefore, it is more challenging but it may be important to extend potential applications of Mg2Si thin films. In the present study, we have explored the synthesis of a Mg2Si film on a sapphire substrate. We chose sapphire because it was transparent over a wide wavelength range and the high-quality, mono-crystalline substrate is commercially available. By carefully adjusting Mg and Si sputter deposition rates to the substrate and by annealing it for two hours in argon gas, we have succeeded in preparing poly-crystalline Mg2Si films with good stoichiometry. Optimum annealing temperature was found from XRD and Raman spectroscopy to be 300-400°C.

2. Experimental Procedure
A single-crystal sapphire (r plane) plate as the substrate has a dimension of 10mm x 10mm x 0.5 mm, which is cleaned ultrasonically for 15 min in acetone before being put into a load-lock chamber. It is then transferred onto a sample heater (one-inch diam., 1200°C max) in a main chamber evacuated down to less than 2 x 10^{-5} Pa. The substrate is then heated at 300°C for 15 min in vacuum to desorb the adsorbed water vapor and hydrocarbons before deposition. Two magnetron sputtering sources (both one-inch diam., movable along the axis) serve to deposit Mg and Si atoms on the substrate at room temperature. The purity of target is 6N for Si and 3N5 for Mg. The Si source (dc powered) is set at 30 mm upper from the substrate, while the Mg source (rf powered) is
set at a distance of 50 mm from the substrate with an angle of 45° from the vertical axis.

The sputter-deposition rate as a function of the discharge power was investigated in the range 10-70 W by setting a quartz crystal deposition monitor at the same place as the substrate. Furthermore, we calculated the thickness of Mg and Si deposition layers required to make a stoichiometric Mg$_2$Si film with a thickness of 1μm (assuming single crystal), to be 720 nm and 310 nm, respectively. From these results, we determined the deposition and annealing procedure as follows: First, the Si source is operated at 50W for 28 min to make a 310 nm layer; then, the Mg source is operated at 30 W for 24 min to superimpose a 720 nm Mg layer on the Si layer. The both depositions are done at an argon pressure of 1 Pa. Finally, a Mg/Si bilayer on the substrate is annealed at a temperature in the range 200 – 500°C for two hours in argon gas at 900 Pa. When the sample is cooled down to 100°C after annealing, it is taken out of the chamber. The synthesized sample is characterized with a x-ray diffractometer, a Raman microscope, a scanning electron microscope-energy dispersive X-ray spectrometer (SEM-EDS), a stylus profiler, and a spectral transmittance measurement system.

3. Experimental Results and Discussion

From x-ray diffraction profiles and Raman spectra of synthesized samples, we found the optimum temperature for the Mg$_2$Si synthesis was in the range 300-400°C (it will be discussed later). The sample SN199 at an annealing temperature of 350°C was cleaved and its cross section was observed with SEM. Furthermore, the elemental composition on the top surface of the sample was measured with EDS. The results are shown in Fig. 1.

![Fig. 1. Cross-sectional SEM view and SEM-EDS spectrum of a synthesized sample SN199.](image)

A columnar structure oriented vertical to the substrate is clearly observed. The thickness is evaluated to be between 1.2μm and 1.3μm from observation by SEM and stylus profiler. The elemental ratio of Mg to Si, 1.98 to 1 from EDS is very close to the stoichiometric ratio of 2 to 1. From these results, the thickness and elemental composition of the synthesized film are considered to be as expected.

The x-ray diffraction pattern of SN199 is shown in Fig. 2. Strong peaks are mainly from the sapphire substrate. A Mg$_2$Si (111) peak at 2θ=24.25° and its higher order peaks, (222), (333) and (444) with less intensities are identified; other Mg$_2$Si peaks such as (220) peak are much weaker than (111) peak. These results are different from those observed earlier for the Si substrate [3,4,6,7]. Figure 3 shows microscopic Raman spectra of SN199 and of a Mg$_2$Si bulk single crystal for
reference. The exciting laser has a wavelength of 532 nm and a spot size of 80μm on the sample surface. The spectra are obtained at different 5 points (see an insert in Fig. 3) for each sample, and are superimposed in the same figure. Sharp peaks corresponding to Mg$_2$Si phonon modes [9] at 257 cm$^{-1}$ (TO/LO), 348 cm$^{-1}$ (LO) and 696 cm$^{-1}$ (2LO) are clearly observed in the spectrum of SN199, which is quite similar to the one of the Mg$_2$Si bulk single crystal. These results suggest that the Mg$_2$Si film (~1μm in thickness) with excellent crystallinity has been synthesized on the sapphire substrate.

The optical transmittance of the Mg$_2$Si film (SN199) was measured over the wavelength range from 500 nm to 2000 nm. The results are given in Fig. 4. A broad-spectrum (215-2500 nm) deuterium tungsten halogen light source (DT-MINI-2-GS, Ocean Optics) illuminated the center of the sample at right angle through a fiber optics. The transmitted light from the rear surface of the substrate was analyzed with both a visible spectrometer (HR4000, Ocean Optics) and a near-infrared spectrometer (NIRQUEST, Ocean Optics). The optical transmittance of the film,
Fig. 4. Optical transmittance of SN199 and a sapphire substrate for reference.

$T(\text{film})$ was evaluated from the following formula [1]:

$$T(\text{film}) = T(\text{sample}) / T(\text{substrate}),$$  \hspace{1cm} (1)

where $T(\text{sample})$ and $T(\text{substrate})$ are the transmittance of the sample (including the substrate) and the bare substrate, respectively. Two transmittance curves derived from visible and near-infrared spectrometers for the same film have been interconnected at a wavelength of 1000 nm to obtain a single curve over the whole wavelength range. An oscillation seen on $T(\text{film})$ (solid line) is due to optical interference of the film. After smoothing the oscillation of the curve, we obtain a transmittance curve removing interference (dashed line). From this curve (dashed line), we find strong absorption in the visible region and almost constant transmission (~54%) in the near-infrared region. This result may suggest the existence of an optical band gap $E_g$ though the evaluation of it is in preparation at present.

Earlier studies have revealed the band gap energy of Mg$_2$Si to be in the range 0.6-0.8 eV[1,5]. This energy range corresponds to the wavelength of 1550-2067 nm at the optical absorption edge.

Optimum annealing temperature for the Mg$_2$Si thin film synthesis has been explored in the temperature range 200-500°C from XRD and Raman spectroscopy. Intensities of Mg$_2$Si (111) peak ($2\theta$=24.25°) and Mg (002) peak ($2\theta$=34.40°) from the 0-20 diffraction profiles are plotted as a function of the annealing temperature in Fig. 5. It appears that the Mg$_2$Si peak shows apparent growth in the range 250-400°C and has the largest value in the range 300-350°C (Fig. 5(a)). In contrast, the Mg peak disappears at 300°C or higher while it has a considerable intensity at a temperature lower than 250°C. The intensity of the Raman peak at 257 cm$^{-1}$ which is typical of the Mg$_2$Si crystal is plotted as a function of annealing temperature in Fig. 6. The intensity starts growing at 300°C, has maximum in the range 350-400°C and becomes zero at 450°C or higher. From Figs. 5 and 6, we find the optimum annealing temperature for the Mg$_2$Si thin film synthesis to be in the range 300-400°C.

At a temperature higher than 450°C, we observed no peaks relating to the Mg$_2$Si crystal in XRD and Raman spectra as already shown in Figs. 5 and 6. This result suggests that the Mg$_2$Si crystal was decomposed or suppressed to be composed at these temperatures. Another observation to be noted that a sharp Raman peak appeared at 521 cm$^{-1}$, which is typical of Si crystal, instead of the peak at 257 cm$^{-1}$ for Mg$_2$Si crystal higher than 450°C. A study is going on to explore a possibility that structural change from Mg$_2$Si crystal to Si crystal (may be poly-crystal) happened during annealing at as low as 450°C.
Fig. 5. XRD peak intensity as a function of annealing temperature for (a) Mg$_2$Si (111) and (b) Mg (002).

Fig. 6. Raman peak intensity at 257 cm$^{-1}$ as a function of annealing temperature.

4. Conclusion

A poly-crystalline Mg$_2$Si thin film (~1μm) was successfully synthesized on a single-crystal sapphire substrate. The sputter-deposited Mg/Si bilayer on the substrate was post-annealed at a temperature of up to 500°C for two hours in argon gas at 900 Pa. The optimum temperature for the synthesis was derived from XRD and Raman intensities to be 300-400°C. The synthesized film showed the strong (111) orientation and the optical transmittance suggesting the existence of the band gap. At a temperature lower than 200°C, the film remained metallic; on the other hand, decomposition of Mg$_2$Si was strongly suggested at a temperature higher than 450°C.

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References