Annealing effects on the formation of semiconducting Mg_2Si film using magnetron sputtering deposition*

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Abstract: Semiconducting Mg_2Si films were synthesized on silicon (111) substrates by magnetron sputtering deposition and subsequent annealing in an annealing furnace filled with argon gas, and the effects of heat treatment on the formation and microstructure of Mg_2Si films were investigated. The structural and morphological properties were investigated by X-ray diffraction (XRD) and scanning electron microscopy (SEM), respectively. The results show that the crystal quality of Mg_2Si films depends strongly on the annealing temperature, the annealing time and the deposited magnesium film thickness. Annealing at 400 ℃ for 5 h is optimal for the preparation of Mg_2Si film. XRD and SEM results show that magnesium silicide film with various orientations is formed on the silicon surface because of the interdiffusion and reaction of magnesium with substrate silicon atoms, and the evolution of surface features on growing films is very dependent on the annealing temperature and time.

Key words: thin film; magnetron sputtering; annealing; X-ray diffraction; scanning electron microscopy
DOI: 10.1088/1674-4926/32/8/082002 **EEACC:** 4210

1. Introduction

As one of the ecologically friendly semiconductors, consisting of non-toxic and abundant materials in the earth's crust[1], with an indirect band gap of 0.6–0.8 eV[2], Mg_2Si has attracted much attention in recent years due to its good ohmic contact character with n-type silicon, showing a contact resistivity of 2.2×10^{-7} Ω·cm, which is an order of magnitude lower than that of Al contacts[3]. However, the formation of high quality Mg_2Si film is not easy because magnesium has very high vapor pressure even at 200 ℃[4], and a very low condensation coefficient[2], and Mg_2Si seems to be easy to decompose and oxidise[5−7]. So, only a few such studies have been published. Wittmer *et al.*[8] fabricated Mg_2Si film by laser melting of magnesium film deposited on silicon substrate, but the synthesized layers contained both silicides and silicon crystallites. Mahan *et al.*[2] obtained Mg_2Si films by molecular beam epitaxy (MBE), and they found that the intended reactive deposition of magnesium onto silicon substrate at temperatures from 200 to 500 ℃ resulted in no accumulation of magnesium. There are a few reports of an ion beam sputtering method for the preparation of Mg_2Si films[9, 10], and not much has been reported about the magnetron sputtering method for preparing semiconducting Mg_2Si film on silicon substrate.

In our previous work, the focus of our efforts was on the formation of semiconducting silicide thin film[11−18]. In this work, semiconducting Mg_2Si films are formed directly on silicon (111) substrates using a magnetron sputtering method, and the influences of heat treatment on the formation and microstructure of Mg_2Si film are investigated.

2. Experiment

Silicon (111) wafers (p-type, 8–13 Ω·cm) were degreased with acetone and alcohol in an ultrasonic instrument for 20 min, respectively. Then they were rinsed with deionized H_2O and blow-dried subsequently. Before sputtering deposition of magnesium film onto a silicon substrate, the surfaces of the magnesium target and silicon substrates were cleaned by argon ion sputtering for 10 min in a high vacuum chamber. Ion sputtering is used to rid the surface of contaminants and promote subsequent film adhesion because real surfaces are usually contaminated with adsorbed gases and assorted compound layers. The base pressure of the magnetron sputtering chamber was 3.0×10^{-5} Pa, and the operating pressure was 3.0 Pa. The sputtering power was 80 W and argon (99.999% purity) flow was 20 sccm during the sputtering process. Under these conditions, the deposition rate of magnesium (99.98% purity) by magnetron sputtering was about 10.8 nm/min.

Magnesium films were deposited on silicon (111) substrates at room temperature by magnetron sputtering. Four groups of magnesium/silicon samples were obtained. The magnesium film thickness of the first three groups of magnesium/silicon samples was 280, 380, and 480 nm, respectively, and these were used to study the effects of annealing temperature and deposited magnesium film thickness on the formation of Mg_2Si films. The magnesium film thickness of the fourth

* Project supported by the National Natural Science Foundation of China (No. 60766002), the Special Funds for International Cooperation of the Ministry of Science and Technology of China (No. 2008DFA52210), the Funds of Information Industry Department of Guizhou Province, China (No. 0831), the Natural Science Foundation of Guizhou Province, China (Nos. 2059, 2323), the Guiyang Science and Technology Bureau (No. 15-3), and the Introducing Talents Foundation for the Doctor of Guizhou University (No. 032).

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Received 30 March 2011, revised manuscript received 20 April 2011 © 2011 Chinese Institute of Electronics

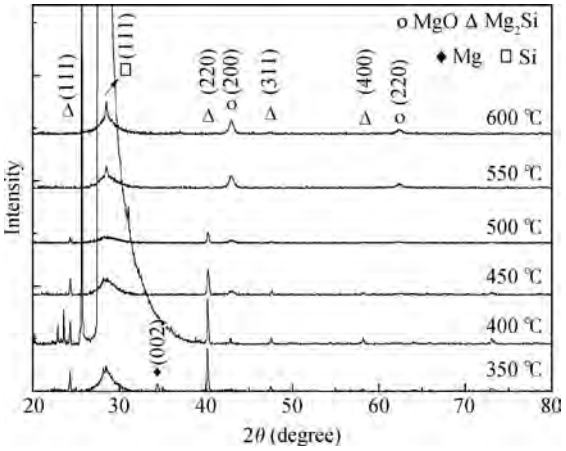

Fig. 1. XRD patterns of Mg_2Si films annealed at various annealing temperatures for 280-nm-thick magnesium film on silicon substrates.

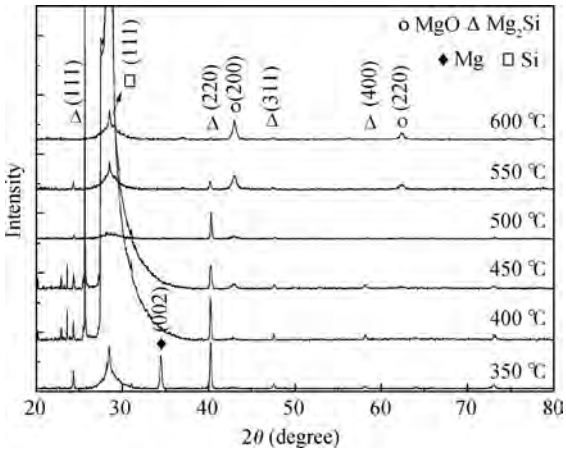

Fig. 2. XRD patterns of Mg_2Si films annealed at various annealing temperatures for 380-nm-thick magnesium film on silicon substrates.

group was also 380 nm, which was used to study the effects of annealing time on the formation of Mg_2Si films. The samples of the first three groups were annealed at 350, 400, 450, 500, 550 and 600 ℃ for 5 h, respectively. The samples of the fourth group were annealed at 400 ℃ for 3.5, 4.5, 5.0, 5.5 and 6 h, respectively.

All of the magnesium/silicon samples were annealed in an argon ambient annealing furnace. The annealing furnace was first pumped to the base pressure of 6.0×10^{-4} Pa, and then it was filled with high purity argon gas at a pressure of about 320 Pa before the furnace was sealed. Annealing in a sealed annealing furnace at an argon pressure of about 320 Pa was used to minimize oxidation of the magnesium layer during high temperature annealing, reduce the loss of magnesium caused by magnesium desorption, and reduce the negative influence of the residual ambient argon impurities due to long time exposure to high temperature[1].

The crystal structure of the films was characterized by X-ray powder diffraction (XRD; model: D8 Advance, Bruker AXS, $\lambda = 0.15406$ nm, θ–2θ scan-mode, step: 0.04°) using CuKα radiation at 40 kV and 40 mA. The surface morphology of the films was characterized by a scanning electron microscope (model: S-4800, Hitachi) at 20 kV with a working distance of 20mm. Phase identification was accomplished by comparing the experimental XRD patterns with the standards compiled by the International Center for Diffraction Data (ICDD). The thickness of film deposited on the silicon substrate was measured by stylus profiler (model: XP-1, Ambios).

3. Results and discussion

3.1. Crystal structure characterization

Figures 1–3 show the XRD patterns of the samples annealed at various temperatures, with deposited magnesium thickness of 280, 380, and 480 nm, respectively. Apart from several Mg_2Si (ICDD Card #35-0773) diffraction peaks, such as (220), (311), (111) and (400) in the 20°–80° region, at a low annealing temperature of 350 ℃, a magnesium (002) (ICDD Card #35-0821) diffraction peak at 34.4° is observed in the XRD pattern in Figs. 1–3. It can be concluded that the magnesium film deposited on the silicon substrate does not form silicide entirely by interdiffusion at a low temperature for 5 h, so all of the synthesized layers contain both magnesium silicide and magnesium crystallites. At an annealing temperature of 400 ℃, the Mg_2Si (220) is still the strongest diffraction peak and the magnesium (002) diffraction peak at 34.4° disappears in Figs. 1–3. At annealing temperatures ranging from 450 to 600 ℃, the intensity of the strongest Mg_2Si (220) peak decreases gradually, and the peaks of Mg_2Si (111), (311) and (400) disappear gradually. Meanwhile, the intensity of the magnesium oxide diffraction peak increases gradually with increasing annealing temperature.

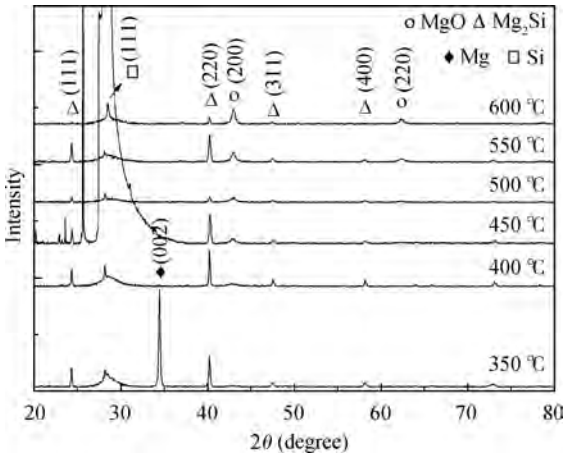

Fig. 3. XRD patterns of Mg_2Si films annealed at various annealing temperatures for 480-nm-thick magnesium film on silicon substrates.

An explanation of the above results is as follows. An increase in annealing temperature accelerates interdiffusion between deposited magnesium atoms and the silicon substrate atoms. Meanwhile, the increase in annealing temperature accelerates the decomposition of Mg_2Si and desorption of magnesium. It was reported that annealing at temperatures of 600–750 ℃ resulted in decomposition of Mg_2Si[5]. There was also a report that the Mg_2Si film remained stable until the annealing temperature reached 450 ℃, then it transformed into MgO, which was attributed to the de-

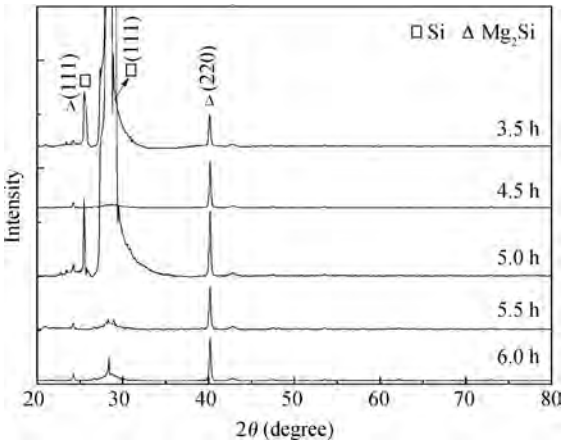

Fig. 4. XRD patterns of Mg_2Si films annealed at 400 ℃ for various annealing times.

composition of Mg_2Si and the oxidization of dissociated magnesium[6]. These results are also confirmed by the experiment done by Vantomme *et al.*[7] who found that a bare 80-nm-thick Mg_2Si polycrystalline film on silicon (111) can be completely removed after annealing at 500 ℃ in vacuum.

In addition, the obvious magnesium oxide diffraction peak is observed in Figs. 1–3, and the intensity of the magnesium oxide becomes strong as the annealing temperature increases. Some reasons for this phenomenon are as follows. The oxygen atoms in the MgO should come from the oxygen annealing atmosphere during annealing. Figures 1–3 reveal the presence of MgO (ICDD Card #45-0946). The following reaction occurs between Mg_2Si and O_2 at 450 ℃[19], $Mg_2Si(s) + O_2(g) \rightarrow 2MgO(s) + Si(s)$, and the following reaction is also possible at high temperature, $2Mg(s) + O_2(g) \rightarrow 2MgO(s)$.

Shown in Figs. 1–3, Mg_2Si diffraction peaks are always strongest and no magnesium oxide diffraction peak is observed if the samples are annealed at 400 ℃, so annealing at 400 ℃ was chosen to further study the effects of the annealing time on the formation and microstructure of Mg_2Si films.

Figure 4 shows the X-ray diffraction patterns of magnesium/silicon samples grown at 400 ℃ for different annealing times. When the annealing time ranges from 3.5 to 6.0 h, the strong Mg_2Si (220) peak is always observed in the XRD patterns as well as the weak Mg_2Si (111) peak in all samples besides the silicon substrate peak. In addition, the intensity of the Mg_2Si peak increases first and then decreases with increasing annealing time. That is to say, the intensity of the Mg_2Si (220) diffraction peak increases with increasing annealing time and reaches its maximum as the sample is annealed for 5 h. When the annealing time is more than 5 h, the intensity of the Mg_2Si (220) diffraction peak becomes weak.

A growth model for the formation of Mg_2Si films by magnetron sputtering and subsequent annealing is proposed as follows. At the initial stage of the sputtering deposition process, magnesium silicide forms at the interface between the silicon substrate and the deposited magnesium layer, and this has been confirmed by the experiments[20, 21]. Then, compressive film stress develops in sputter-deposited film from high energy particle bombardment[20]. Compressive film stress is accumulated

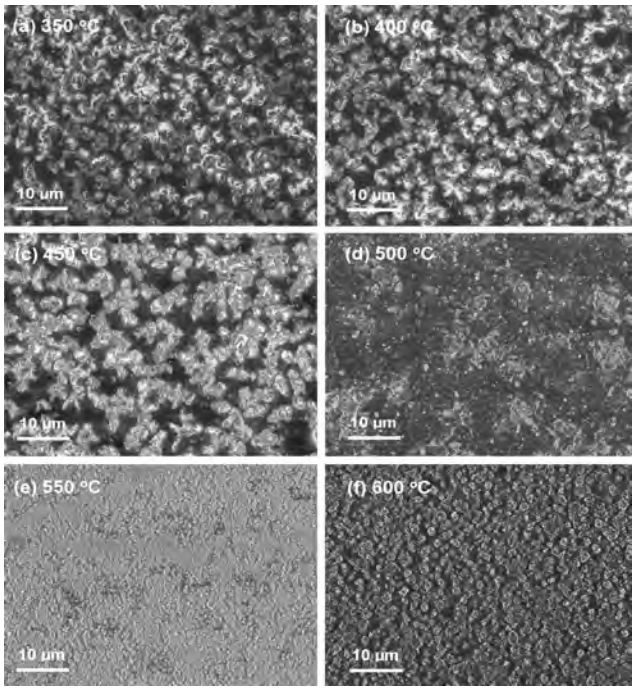

Fig. 5. SEM images of the samples annealed at various annealing temperatures for 5 h.

in the film with increasing film thickness in sputter-deposited magnesium/silicon films[21]. Some fine Mg_2Si grains with various orientations are formed at the interface between the silicon substrate and the deposited magnesium layer. In the subsequent annealing process, more conversion to Mg_2Si takes place to form Mg_2Si films. Since extensive surface diffusion is indispensable for the reaction of magnesium and silicon atoms, fine Mg_2Si grains with various orientations grow in size during the high temperature annealing. As a result of the interdiffusion and reaction of magnesium with silicon atoms, a magnesium silicide film with various orientations is formed on the silicon surface. As shown in Figs. 1–3, the presence of the crystalline diffraction peaks indicates that the films prepared by magnetron sputtering are polycrystalline in nature, which means that the grains may have various orientations. Therefore, Mg_2Si (111), Mg_2Si (200) and Mg_2Si (311) planes are formed together with the preferred Mg_2Si (220) on the Si (111) substrate during annealing.

3.2. Surface morphologies of the samples

Figure 5 shows the SEM images of the magnesium/silicon samples with 380-nm-thick magnesium films annealed at various annealing temperatures for 5 h. As shown in Fig. 5, the surface of the film first becomes smooth with increasing annealing temperature. When the annealing temperature is 350, 400 and 450 ℃, respectively, distributed grains are embedded in the surfaces of the films. When the annealing temperature reaches 500 and 550 ℃, the surface of the film becomes smoother because the higher temperature accelerates interdiffusion between the magnesium atoms and silicon atoms and reduces the defect concentration of the obtained films.

Figure 6 shows the SEM images of the samples annealed at 400 ℃ for various annealing times. XRD data from Fig. 4

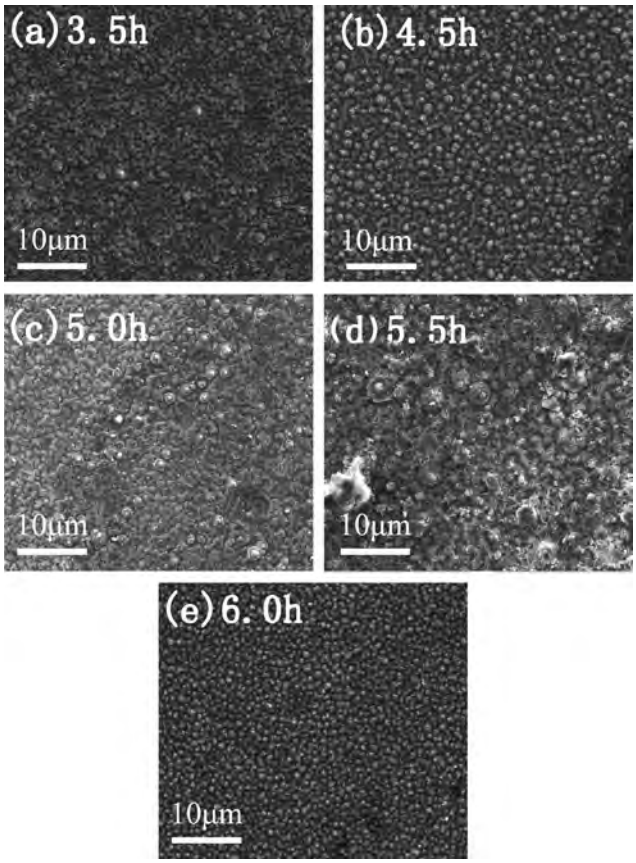

Fig. 6. SEM images of the samples annealed at 400 ℃ for various annealing times.

reveal the formation of magnesium silicide after annealing at 400 ℃ of magnesium film with 380-nm thickness. Rough surfaces are also observed when the samples are annealed at 400 ℃ for 3.5 and 4.5 h. For the sample annealed for 5 h, the surface becomes dense and smooth. For the film annealed for 5.5 h, the surface appears still relatively flat, but the grains are still identifiable. When the annealing time is increased to more than 6 h, more grains can be observed again.

Figures 5 and 6 show that a very rough surface with three-dimensional island-like features can be observed in the specimens. The growth of thin films prepared by sputtering deposition on well-oriented single-crystal substrates is usually governed by island growth[22]. The evolution of surface features on growing films is very much dependent on the annealing temperature, the time and subsequent atomic surface diffusion. Surface diffusion is a transport mechanism of importance in thin films because of their large surface-to-bulk ratio. This mechanism plays an important role in film nucleation and growth processes. In the metal-rich silicides, the metal is often observed to be the dominant mobile species, whereas in the mono- and disilicides, silicon is the diffusing species[23]. It has been reported that magnesium atoms are the predominant moving species in diffusion in Mg_2Si formation[24]. The magnesium-rich silicides probably form by the mechanism of bond breaking through rapid interstitial migration of metal magnesium through the silicon lattice, as has been suggested[23].

At elevated temperatures, both surface and bulk diffusion allow atoms to access equilibrium lattice sites, fill voids, and enlarge grains. At the initial stage, the higher the annealing temperature, the larger the grain sizes obtained. The lateral grain size is expected to increase with increasing surface mobility of the adsorbed species. As a result, deposits with well-defined large grains are formed at high temperatures[22]. Meanwhile, high annealing temperatures facilitate growth by promoting island coalescence. The coalescence process frequently appears to be liquid-like with islands merging and undergoing shape changes after the fashion of liquid droplet motion. Continued coalescence results in the development of a connected network with unfilled channels in between. Finally, even the voids fill in completely and the film is said to be continuous, which is evident in Fig. 5.

The variation of the annealing time is supposed to lead to a change in the crystallite quality—the size, the lattice parameter uniformity and the stoichiometry. Consequently, the increase in the annealing temperature leads to an increase in bulk silicon diffusion and could destroy cluster layers in the silicon matrix, but only the long annealing time at fixed high temperature could support the crystallization process[22], so the grain sizes of the films increase as the annealing time increases.

However, as shown in Figs. 5 and 6, while annealing-induced surface smoothing occurs during film growth, another interesting roughening of the surface topography is observed again under higher annealing temperatures and longer time conditions. Although the details are not clearly understood, we think the reasons for the above results are as follows. (1) At sufficiently high kinetic energies, the surface mobility is reduced due to the penetration of the species into the substrate, resulting in a smaller grain size[22], and the composite island generally reassumes a crystallographic shape with time[23]. (2) Based on the above discussions, decomposition of Mg_2Si film may be responsible for the recurrence of small grains.

4. Conclusion

Mg_2Si film on silicon (111) substrates has been prepared successfully by magnetron sputtering. The influence of heat treatment on the formation and microstructure of Mg_2Si film has been investigated. The crystal quality of Mg_2Si films depends strongly on the annealing temperature and time as well as the deposited magnesium film thickness. At a low annealing temperature of 350 ℃, the synthesized layers contain both magnesium silicide and magnesium crystallites. However, magnesium oxide is observed to form with an increase in annealing temperature above 550 ℃, and a higher annealing temperature causes decomposition and oxidation of Mg_2Si, so it is necessary to optimize the heat treatment process to obtain high quality Mg_2Si film on a silicon substrate. XRD patterns show that annealing at 400 ℃ for 5 h is optimal for preparing Mg_2Si film. XRD and SEM results also show that the formation of the Mg_2Si phase is caused by interdiffusion between deposited magnesium atoms and silicon substrate atoms.

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