Interfacial microstructures of rf-sputtered TiNi shape memory alloy thin films on (100) silicon

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ABSTRACT

Interfacial microstructures of TiNi thin films rf sputtered on to Si(100) and post-annealed at 400–700°C for 30 mins have been investigated using analytical and high-resolution transmission electron microscopy. For annealing temperatures below 600°C, a very thin amorphous (Si, O)-rich layer is observed at the interface. Ni atoms are the primary diffusing species and NiSi₂ forms triangularly and epitaxially towards the Si substrate. TiNi films initially crystallize after 30 min at 500°C. Si and Ti atoms begin to migrate in specimens annealed at 600°C for 30 min. At this temperature, a near-Ti₄Ni₄Si₇ phase in triangular NiSi₂ and a near-TiNiSi phase in the TiNi film are simultaneously nucleated and grown at the interface. For the specimens annealed at 700°C for 30 min, two layers of Ti₄Ni₅Si₂ and TiNiSi form at the interface with the sequence TiNi/TiNiSi/Ti₄Ni₅Si₂/Si. Triangular NiSi₂ islands are now embedded in the Ti₄Ni₅Si₂ layer. A mechanism of interfacial microstructure evolution is proposed to explain the temperature effect on the interfacial reaction layers between the TiNi film and the Si(100).

§ 1. INTRODUCTION

1996); thus many efforts have been made to sputter good-quality TiNi thin films (Gisser et al. 1992, Ishida et al. 1993, 1996, 1997, Chen and Wu 1999, Wu et al. 2000). During the fabrication processes, the interfacial reaction between films and substrate becomes significant under thermal treatments for crystallization (Gisser et al. 1992, Chen and Wu 1999), ageing (Ishida et al. 1996, 1997) and stress relaxation (Zhang and Grummon 1997). This will seriously affect the properties of TiNi shape memory alloys. Therefore, it is important to investigate the interaction of the film-substrate interface at higher temperatures.

Several papers have discussed the interfacial interaction for the Ti or Ni monolayer and TiNi or Ni/Ti bilayers on Si substrates (Horache et al. 1989, Setton et al. 1989, Sieber et al. 1991, Falke et al. 1997), but this is indeed different from the TiNi/Si-substrate case. To the best of our knowledge, only two studies have been reported which are related to the TiNi/Si-substrate system (Hung and Mayer 1986, Stemmer et al. 1997). Hung and Mayer studied the Ti$_{52}$Ni$_{48}$ film on Si(100). The Ti$_{52}$Ni$_{48}$ film crystallizes after 30 min at 450°C and forms a ternary TiNiS$_2$ compound after 30 min at 625°C (Hung and Mayer 1986). In addition, the interfacial reaction between the Si(100) substrate and nearly equiatomic TiNi film reveals several phases, including a Ti$_2$Ni compound, a nickel silicide and a ternary titanium nickel silicide (Stemmer et al. 1997). Nevertheless, the data are merely available at the 525°C annealing condition and thus could not provide details for the other annealing temperatures.

In this study, near-equiaxial TiNi thin films were rf sputtered on to a Si(100) wafer and then annealed at temperatures between 400 and 700°C for 30 min. The reaction phases and microstructures at the TiNi-Si interface resulting from the post-deposition thermal anneal are investigated. An interfacial evolution mechanism well fitted to the experimental observation is also proposed.

§2. EXPERIMENTAL PROCEDURE

Near-equiaxial TiNi thin films were sputtered on to the surface of cleaned and oxide-etched Si(100) wafers, using a rf magnetron gun in an ultrahigh ($1 \times 10^{-7}$ Torr) chamber. The sputtering conditions were as follows: sputtering pressure, 50 mTorr; target-substrate distance, 50 mm; dc power, 200 W; deposition rate, about 5 Å s$^{-1}$. The target used in this study was a Ti$_{49}$Ni$_{51}$ disc of 2 inch diameter. The sputter-deposited specimens with thickness of about 1 μm were sealed in evacuated quartz tubes, thermally annealed at 400, 500, 600 and 700°C for 30 min and then furnace cooled to room temperature.

The annealed TiNi films were used to observe the cross-sectional microstructures of the TiNi-Si interface. Cross-sectional transmission electron microscopy (TEM) specimens were fabricated by grinding, dimpling and ion milling at 5 kV to perforation. A sector speed-controlled whisper-lock of a Gatan DuoMill at liquid-N$_2$ temperature was used to minimize the effects of different ion-milling rates of TiNi and Si in cross-sectional TEM specimens. Microstructure observation was performed using a JEOL model 4000 FX transmission electron microscope operated at 400 kV with 2.6 Å point-to-point resolution and a JEOL field emission transmission electron microscope model 2010F operated at 200 kV with 1.3 Å point-to-point resolution. A dedicated energy-dispersive spectroscopy (EDS) system was employed with both transmission electron microscopes.


§3. RESULTS

3.1. As-deposited TiNi/Si and specimen annealed at 400°C for 30 min

The as-deposited TiNi films are amorphous with a columnar structure growing normal on to the Si substrate (Chen and Wu 1999, 2000, Wu et al. 2000). The composition of the as-deposited TiNi film is about Ti_{50.40}Ni_{49.60} (in atomic percentages) with a slight fluctuation.

The cross-sectional TEM image of a TiNi/Si specimen annealed at 400°C for 30 min is shown in figure 1(a), and the selected-area diffraction pattern (SADP) of the Si substrate near the interface of figure 1(a), areas C and D, is shown in figure 1(b). The composition of the TiNi film is about Ti_{50.40}Ni_{49.60} (in atomic percentages) with a slight fluctuation. The composition of the Si substrate near the interface is shown in figure 1(c). The EDS of the triangular C is shown in figure 1(d).

Figure 1. (a) The cross-sectional TEM image of a specimen annealed at 400°C for 30 min. Areas A, B, C and D are the TiNi film, (the Si, O)-rich amorphous layer, the triangular NiSi_{2} and the Si substrate respectively. (b) The SADP of the Si substrate. (c) The EDS of the triangular C. (d) The high-resolution TEM image of the NiSi_{2}–Si interface.
The TiNi film in figure 1(a) (area A) is still amorphous. Figure 1(c) is the EDS result of the triangular reaction product (area C) in figure 1(a). Obviously, these triangular products are the NiSi$_2$ compound which has undergone solid solution with a very little Ti.

Figure 1(b) is the SADP of the $\langle 011 \rangle_{Si}$ zone axis. It is also the SADP of the $\langle 011 \rangle_{NiSi_2}$ zone axis. This is due to the epitaxial stress-free growth of NiSi$_2$ on to the Si(100) substrate, as shown in figure 1(d). The lattice constant of Si (diamond structure) is $d = 0.5430$ nm and that of NiSi$_2$ (fcc structure) is $d = 0.5416$ nm. Therefore, the SADPs of $\langle 011 \rangle_{Si}$ and $\langle 011 \rangle_{NiSi_2}$ will coincide with each other owing to very little lattice mismatch (0.25%). The crystal lattice of this disilicide is constructed by replacement involving one Ni atom at (000) and two Si atoms at $(\pm \frac{1}{4}, \pm \frac{1}{4}, \pm \frac{1}{4})$ (Falke et al. 1997). In figure 1(a), the greatest depth of triangular NiSi$_2$ measured from the TiNi–Si interface is about 20 nm. Layer B of figure 1(a) is suggested to be a 2–3 nm (Si, O)-rich layer identified as amorphous (Stemmer et al. 1997).

3.2. Annealing at 500°C for 30 min

Figure 2(a) shows the cross-sectional TEM image of a TiNi/Si specimen annealed at 500°C for 30 min and figures 2(b) and (c) are the SADPs of the silicon substrate and TiNi film near the interface in figure 2(a). As seen in figure 2(a), triangular NiSi$_2$ achieves the greatest depth from the TiNi–Si interface, which is approximately 45 nm. In figure 2(a), most of the epitaxial growth interfaces between NiSi$_2$ and Si are $\{111\}$ planes, as indicated at A, but occasionally $\{100\}$ planes can also be observed, as shown at C. Position B in figure 2(a) is the location where perforation can occur most easily during ion milling. Position B is located at the
Figure 2. (a) The cross-sectional TEM image of a specimen annealed at 500°C for 30 min. Areas B, A and C are a perforation, the \{111\} plane and the \{100\} plane of triangular NiSi₂ respectively. (b) The SADP near the interface. (c) Ring patterns. Rings 1–4 correspond to the TiNi B2 phase, but other rings may come from the Ti₂Ni or Ti₂Ni₃Si compounds.
intersection of NiSi2, the Si substrate and the TiNi film, where the largest retained stress may be induced after annealing. In figure 2(a), the amorphous layer 2–3 nm thick still exists.

In figure 2(b), the SADPs of \( (011)_{Si} \) and \( (011)_{NiSi2} \) are superimposed on the ring pattern of TiNi film near the TiNi–Si interface. The ring pattern in figure 2(b), identified as a B2 structure, is suggested to be the \( Ti_{50}Ni_{50} \) B2 austenite phase, as shown in figure 2(c). This ring pattern demonstrates that the amorphous TiNi film just begins to crystallize after 30 min at 500°C. In figure 2(b), the most remarkable ring of TiNi B2 ring pattern is the \( (011) \) plane \( (d = 0.214 \text{ nm}) \). There are other remarkable rings near the \( (011) \) ring of the B2 phase possibly coming from the \( (511) \) ring of the \( Ti_{2}Ni \) phase \( (d = 0.217 \text{ nm}) \), and/or the (220) ring \( (d = 0.21 \text{ nm}) \) or the (115) ring \( (d = 0.22 \text{ nm}) \) of the \( Ti_{2}Ni_{3}Si \) phase (Stemmer et al. 1997). As indicated by Stemmer et al., the \( Ti_{2}Ni \) and \( Ti_{2}Ni_{3}Si \) phases are formed at the TiNi film–Si interface annealed at about 525°C for 30 min.

3.3. Annealing at 600°C for 30 min

Figure 3(a) shows the cross-sectional field emission TEM image of a TiNi/Si specimen annealed at 600°C for 30 min. Areas of triangular NiSi2 are still growing and their greatest depth from the TiNi–Si interface approaches 120 nm. Obviously, the (Si, O)-rich amorphous layer is still located between the TiNi film and Si substrate, but its thickness grows from 2–3 nm to about 5 nm at position B. Moreover, no triangular NiSi2 grows from there, implying that the thick amorphous layer may retard the diffusion of Ni atoms from the TiNi film on to the Si substrate. Area D in figure 3 shows the perforation site during ion milling, which is similar to that observed in figure 2(a). However, in figure 3, there are many more perforations and the sizes are larger. This feature may result from the fact that more retained stress exists in the specimen annealed at higher temperatures at the intersection of NiSi2, the Si substrate and TiNi film.

The compositions of positions 1–5 in figure 3(b) are detected using the EDS system of the field emission transmission electron microscope. The EDS data show that positions 1 and 2 have the average composition \( Ti_{22.60}Ni_{24.34}Si_{53.06} \) whereas the average composition of positions 3–5 is \( Ti_{31.55}Ni_{32.23}Si_{36.22} \). The former is close to the composition of the \( Ti_{4}Ni_{4}Si_{7} \) Laves phase and the latter approaches to that of the TiNiSi Laves phase (Settom and Van der Spiegel 1988). Figure 3 shows that the \( Ti_{4}Ni_{4}Si_{7} \) compound nucleates between the amorphous layer and NiSi2 and then grows into the triangular NiSi2 and the Si substrate. On the contrary, the TiNiSi compound forms between the amorphous layer and the TiNi film and then grows towards the TiNi film.

3.4. Annealing at 700°C for 30 min

Figure 4(a) shows the cross-sectional TEM image of a TiNi/Si specimen annealed at 700°C for 30 min. The compositions of layers A and B, and island C of figure 4(a) have been identified using the EDS system of the transmission electron microscopy, as shown in figure 4(b). Obviously, layer A is TiNiSi, layer B is \( Ti_{4}Ni_{4}Si_{7} \) and island C is NiSi2 which has undergone solid solution with several Ti atoms. The thicknesses of layers A and B are more than 0.5 and 0.3 μm respectively. In figure 4(a), \( Ti_{4}Ni_{4}Si_{7} \) has now grown to form a layer embedding the triangular NiSi2. The (Si, O)-rich amorphous layer, originally formed at the TiNi–Si interface annealed at a lower temperature, is not present in figure 4(a). This feature may cause
Figure 3. (a) The cross-sectional TEM image of a specimen annealed at 600°C for 30 min. Areas A, B, C, D and E are the TiNi film, the (Si, O)-rich amorphous layer, the NiSi₂, a perforation and the Si substrate respectively. (b) The same as (a), but now a phase close to that of the TiNiSi compound forms at positions 3–5 and another phase close to that of the Ti₄Ni₄Si₇ compound forms at positions 1 and 2.
Figure 4. (a) The cross-sectional TEM image of a specimen annealed at 700°C for 30 min. Areas A, B and C are TiNiSi, Ti₄Ni₄Si₇ and NiSi₂ respectively. (b) The EDS data of areas A, B and C.
Interfacial microstructures of TiNi thin films

(a) As-deposited

(b) 400°C x 30 min Annealing

(c) 500°C x 30 min Annealing

(d) 600°C x 30 min Annealing

(e) 700°C x 30 min Annealing

Figure 5. Schematic diagrams of the microstructural evolution of interfacial reaction layers of TiNi/Si annealed at 400–700°C for 30 min.
the Ti and Si atoms to diffuse more quickly. At the same time, the formation of the Ti4Ni4Si7 compound in or around triangular NiSi2 may suppress the growth of triangular NiSi2, as the depth of NiSi2 is about 100 nm in figure 4(a), the same as in figure 3(a).

§ 4. Discussion

The microstructural evolution of interfacial reaction layers of TiNi film/Si(100) annealed at 400–700°C for 30 min is schematically shown in figure 5. Figure 5(b) shows that the triangular NiSi2 begins to grow after 30 min at 400°C from the interface to the Si because the Ni atoms initially migrate from the TiNi film to the Si. The (Si, O)-rich amorphous layer becomes a good diffusion barrier to Ti and Si at low temperatures. This is because the formation of nickel silicide at the Ni-Si-substrate interface is less sensitive to the O-rich layer than the formation of titanium silicide in the Ti/Si-substrate system (Horache et al. 1989). The NiSi2 formation, instead of NiSi or Ni2Si in this study, may be due to the (Si, O)-rich layer which reacts against the diffusion of Ni atoms, leading to a lower Ni supply rate, which facilitates the formation of the Si-rich silicide, NiSi2. According to the Ni–Si phase diagram (Brandes 1983), NiSi2 is the most Si-rich stable intermetallic compound in the Ni–Si system. As the sample is annealed at 500°C for 30 min, as indicated in figure 5(c), triangular NiSi2 grows into the Si substrate and the TiNi film begins to crystallize as a Ti50Ni50 B2 phase because the crystallization temperature of nearly equiatomic TiNi thin films is around 500°C (Chen and Wu 1999, 2000). When the annealing condition is changed to 600°C, as shown in figure 5(d), Ti and Si atoms obtain the required energy to penetrate the (Si, O)-rich amorphous layer, and some positions at the TiNi–Si interface reveal ternary Ti–Ni–Si compounds. A near-Ti4Ni4Si7 compound nucleates at the interface and grows into the triangular NiSi2 and the Si substrate, and a near-TiNiSi compound also nucleates at the interface and grows into the TiNi film. This means that Si and Ti atoms initially migrate at approximately 600°C. Figure 5(e) shows that the Ti4Ni4Si7 and TiNiSi ternary compounds have formed two layers between the crystallized TiNi film and the Si substrate. Areas of triangular NiSi2 are embedded in the Ti4Ni4Si7 layer and formed isolated islands. The (Si, O)-rich amorphous layer disappears at this interface. The Ti4Ni4Si7 is located near the Si substrate because of the abundant Si constituent; on the contrary, TiNiSi grows on the side of the TiNi film owing to the limited Si supply. The diffusion bonding of a bulk thick Si(100) single crystal and bulk Ti50Ni50 alloy at 960°C for 6 h also reveals a similar result, that is TiNiSi forms near the Ti50Ni50 bulk alloy but Ti4Ni4Si7 forms near the bulk Si crystal with the thickness of TiNiSi being much less than that of Ti4Ni4Si7 (Wu 1998).

§ 5. Conclusion

The rf-sputtered TiNi film on Si(100) was annealed at 400–700°C for 30 min and their interfaces are studied using TEM + EDS and field emission TEM + EDS analyses. Experimental results show that, for annealing temperatures below 600°C, Ni atoms are the main species diffusing at the TiNi–Si interface and the NiSi2 compound forms triangularly and grows epitaxially towards the Si substrate. The as-deposited TiNi films are amorphous, but they initially crystallize after 30 min at 500°C. For annealing temperatures higher than 600°C, as well as Ni atoms, Si and Ti atoms also migrate. In certain areas of the TiNi/Si interface annealed at 600°C for 30 min, a ternary compound close to the composition of Ti4Ni4Si7 forms into trian-
Interfacial microstructures of TiNi thin films

Regular NiSi₂ and the Si substrate while a ternary compound close to the composition TiNiSi grows in the TiNi film simultaneously, with the former having a thickness of approximately 15–35 nm and the latter about 50 nm. For the TiNi–Si interface annealed at 700°C for 30 min, the Ti₄Ni₄Si₇ compound grows and forms a layer with a thickness of more than 0.3 μm. The NiSi₂ compound is now embedded in this layer as isolated islands. The TiNiSi compound also grows and forms a layer of 0.5 μm thickness. A (Si, O)-rich amorphous layer with a thickness of 2–3 nm is also observed in specimens annealed at 400–600°C but disappears in those annealed at 700°C. From the observations of this study, microstructural evolution is proposed to explain the effect of temperature on the formation of interfacial TiNi film–Si(100) reaction layers of annealed at 400–700°C for 30 min.

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