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Adhesion and interfacial structure of magnetron sputtered TiNi films on Si/SiO_2 substrate

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Abstract

Shape memory alloy TiNi films were prepared on Si and Si/SiO₂ by co-sputtering of TiNi target (Ti 50 at.% and Ni 50 at.%) and Ti target (99.999 at.%). When comparing Si/TiNi with Si/SiO₂/TiNi, the addition of SiO₂ sandwich layer did not result in significant change in the crystalline structures and shape memory properties. The SiO₂ sandwich layer served as an effective diffusion barrier in preventing formation of interfacial titanium silicide at the expense of film adhesion. As revealed by X-ray photoelectron spectroscopy, under the same conditions, the interfacial diffusion zone in Si/TiNi system was approximately 120 nm while in Si/SiO₂/TiNi system the diffusion zone was only approximately 30 nm—a four-fold reduction in inter diffusion. Meanwhile, the scratch adhesion testing registered a sharp drop in adhesion of the film from 170 mN in Si/TiNi system to 60 mN in Si/SiO₂/TiNi system.

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1. Introduction

TiNi-based shape memory alloy (SMA) thin films are promising for numerous applications, and great effort has been made to produce TiNi based thin films using the sputtering technique [1-7]. These vacuum deposited TiNi films generally show fine-grained structure, high surface reactivity and sensitivity. Usually, films deposited at room temperature are amorphous and subsequent annealing is necessary to crystallize the film. Delamination of TiNi films on Si is sometimes observed owing to thermal, intrinsic and phase transformation stresses [8,9]. For TiNi films deposited on Si substrate, there exist interfacial diffusion and chemical interactions at the interface whereby titanium and nickel silicides may form during high temperature deposition or post-deposition annealing [10-12]. These interfacial reaction products could be complex, heterogeneous and metastable. Since the TiNi film thickness required in MEMS applications are usually a few microns, a relatively thin reaction layer could have significant adverse effect on

adhesion and shape memory properties. A thermally grown SiO₂ layer is recognized as an effective diffusion barrier layer. The TiNi/SiO₂ interface adherence is good and no spallation is observed because of the formation of 200–300 nm untransformed austenite phase which can accommodate the strain through absorbing the elastic energy [2,13]. Thus, TiNi/SiO₂/Si system has been used as a gate for metal-on-silicon capacity sensors [14] where SiO₂ acts as an electrical and thermal insulating layer to prevent silicide formation, and also as a sacrificial layer in surface micromachining processes. However, this investigation reveals that the inclusion of the SiO₂ layer does not favor TiNi's adhesion though the interdiffusion is effectively blocked.

2. Experimental details

Ti51.2Ni48.8 films with a thickness of 4 μ m were prepared by co-sputtering of a TiNi target (of atomic ratio of 50/50) at RF 400 W and a pure Ti target at DC 70 W on a 4-inch silicon (100) substrate with and without 200 nm thermally grown SiO₂ layer. All the substrates were heated to 723 K during deposition. Substrate holder was rotated during deposition for uni-

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Fig. 1. Curvature measurement results for TiNi films deposited onto Si and SiO₂ surface showing the martensite phase transformation.

formity. The base pressure of main chamber was 1×10^{-7} Torr. The argon pressure during deposition was 2.3 mTorr. Film composition was determined by energy dispersive X-ray microanalyzer (EDX). The martensitic transformation behaviors were evaluated using curvature methods. Curvature changes of film-deposited Si wafers were measured using a Tencor FLX-2908 laser system at a heating and cooling rate of 1 K/min. The crystallinity of the films was determined by X-ray diffraction (XRD) (Cu K_{α} 40 kV/30 mA). Interfacial adhesion of the TiNi film surface was assessed using a SHIMADZU SST-101 scanning scratch tester. A stylus of 15 µm tip radius was used at a load increased stepwise to a full load of 500 mN. During the scratch operation, the forward speed was set at 2 μ m/s and the amplitude of scanning was 50 µm. X-Ray photoelectron spectroscopy (XPS) analysis was performed on TiNi/Si and TiNi/ SiO₂ interfaces using a Kratos AXIS spectrometer with monochromatic Al Ka (1486.71 eV) X-ray radiation. TiNi film was peeled off from Si and SiO₂ substrates, and the peeled-off interfaces were analyzed using XPS for interfacial chemistry. The pressure of the analysis chamber was lower than 10^{-7} Pa, which increased to approximately 5×10^{-5} Pa during ion bombardment. Wide-scan spectra in the 1100 to -4 eV binding energy range were recorded in 1 eV step for all samples. Detailed spectra of the core level lines of different elements were recorded in 0.1 eV steps. For elemental depth profiling of the interfacial structure, an ion gun (Kratos MacroBeam) of 4 keV energy was used at a sputtering rate of 0.05 nm/s with high purity Ar gas.

3. Results and discussions

3.1. Shape memory and adhesion evaluation

The phase transformation behaviors of the TiNi films on Si and on Si/SiO₂ are shown in Fig. 1. The responses



Fig. 2. XRD results for the TiNi films deposited on Si and SiO₂ layer.

are basically identical: Both curves show a one-stage transformation corresponding to martensite (B19') to austenite (B2) transformation during heating and a two-stage transformation during cooling corresponding to transformations among martensite, R-phase and austenite phases. There are minor differences in phase transformation temperatures, and on SiO₂ the film shows relatively lower recovery stress (the difference between the maximum and lowest stress values).

Fig. 2 plots the XRD results. Martensite phase (B19') is dominant for both films. There are some differences between the preferred orientations of martensite phases for two films. Directly on Si, (002) B19' is the preferred orientation of martensite structure, since the Si substrate is (100) orientation. On amorphous SiO₂ layer, however, (111) B19' becomes its preferred orientation.

In scratch test, the 'lower critical load' or the normal load at which the first damage incurs is widely used as a measure of the adhesion strength. Fig. 3 depicts the



Fig. 3. Scratch results showing the adhesion failure of TiNi films deposited on Si and SiO_2 surface.



Fig. 4. Scratch morphology of adhesion failure for TiNi films on (a) SiO_2 and (b) Si.

scratch behavior of the films. On SiO₂ surface, a sudden increase in frequency output occurs as the normal load is increased to above 60 mN, indicating that the adhesion failure occurs at 50 mN (or the lower critical load is 60 mN). Further increase of load generates more damages. At a normal load of 160 mN, spallation occurs and the large spallation is readily seen under optical microscopy as shown in Fig. 4a. Whereas for TiNi film on Si substrate, it is clear that the lower critical load is 170 mN, and there is no apparent damage in the film as shown in Fig. 4b. Several tests were performed at different TiNi/Si and TiNi/SiO₂ samples, and the results are similar-adhesion failure of TiNi/Si occurs at approximately 150–180 mN, whereas TiNi/SiO₂ occurs at approximately 60-90 mN. It is obvious that the TiNi film adheres much better on Si than on SiO₂. One can easily feel the difference when peeling off the TiNi film from the two substrates.

3.2. TiNi/Si interfacial characterization

TiNi films were peeled off from Si substrate, and the elemental composition on both 'TiNi-side' and 'Si-side'

surfaces were immediately measured using XPS. The atomic concentration evolution from the interface into TiNi layer is shown in Fig. 5. The profiles show three different regions. The first region is near the Si/TiNi interface, and is characterized by C and O contamination (a layer of a few nanometer thick). The second region presents Si diffusion layer (approximately 30- to 40-nm thick), and the last is the bulk TiNi film. Results indicate that there is significant inter-diffusion of Si atoms into TiNi films, and silicon can be detected 60 nm beneath film surface.

Fig. 6a-c shows high-resolution Si 2p, Ti 2p and Ni 2p spectra changing with depth into TiNi films. Fig. 6a shows the Si 2p peak evolution with depth. On the surface (the first curve at the bottom), the peak component at approximately 99-100 eV corresponds to Si-Si bonds. There is also a strong contribution from silicon oxides (SiO_2) in the Si 2p spectrum at a binding energy at approximately 103-104 eV. With increase of depth into TiNi films, the Si 2p component shifts gradually to lower binding energy relative to that of the Si-Si bond due to the formation of Si-Ti or Si-Ni bond structures, because of the higher electrogativity of Si with respect to Ti or Ni (Si: 1.8; Ti: 1.5; Ni: 1.8 [15]). The chemical shift of Si 2p core levels at binding energies of -0.6 and -1.1 eV relative to the Si-Si bond corresponds to the formation of TiSi and Si in solution of Ti [10]. In brief, there are four distinct chemical environment for Si atoms in this interfacial diffusion region, namely: (1) silicon oxide (Si-O bond) at surface; (2) silicon in bulk materials (Si-Si bond); (3) Si in Ti–Si or Ni–Si compounds in the intermediate layer; and (4) Si as a solution in TiNi films.

Fig. 6b,c show Ti and Ni 2p peaks' evolution with depth. The intensities of both Ti and Ni peaks increase with depth. Ni mainly exists in the metallic state with



Fig. 5. Interfacial atomic element distribution in TiNi films peeled off from Si substrate. The zero depth was the location of the Si/TiNi interface.



Fig. 6. Si 2p, Ni 2p and Ti 2p spectra evolution with depth into TiNi interface peeled from Si substrate (a) Si 2p, (b) Ni 2p and (c) Ti 2p.

broad satellite peaks probably due to sputter-damaged crystallites. No significant peak shift for Ni 2p peaks is observed. Since the electronegativity of Si with Ni are almost the same, thus, even though there is nickel silicide formation, there may not be apparent change in chemical state. For Ti 2p spectra, on the surface, apart from metallic Ti peak, there is some content of TiO_2

peak due to oxygen contamination. Beneath the surface, Ti mainly exists as metallic, and the high intensity between the 2p 2/3 and 2p 1/2 peaks is due to the presence of shake-up satellite structures [16]. The difference in relative satellite intensity may be a consequence of sputter-damaged crystallites. It is proposed that ion beam damage of TiNi could cause alternations in the bond structures of these materials and leads to a higher proportion of the Ti 2p photoelectrons being involved in shake-up processes [17]. The presence of Ti–Si bonds for Ti 2p peak could be at approximately 454.8 eV [18], but overlaps with TiO and shake-up satellite structures, thus it is difficult to calculate the percentage of Ti–Si bonds forming Ti 2p peak evolution.

The composition depth profile of Ti, Ni and Si into the Si interface was also plotted in Fig. 5. Again, three different zones are observed: (1) surface contamination layer of approximately 10 nm; (2) TiNi diffusion layer of approximately 60 nm; and (3) Si substrate. In TiNi diffusion layer, both Ti and Ni contents first increase to a maximum (approx. 15 at.% at a depth of 10 nm) then gradually decrease. Trace amount of Ti and Ni elements can be found as deep as 60-70 nm. In brief, there is significant inter-diffusion between Si substrate and TiNi films, and the total intermixing layer is approximately 120 nm (60 nm into TiNi layer and 60 nm into Si substrate). Also, XPS results confirm that there is the formation of titanium silicides.

3.3. TiNi/SiO₂ interfacial characterization

Composition depth profiling into TiNi interface peeled from Si/SiO_2 gives rise to Fig. 7. On the film surface, large amount of oxygen can be observed. About 20 at.% of Si content can be observed. Ti elements show relatively high concentration, and Ni remains at very



Fig. 7. Interfacial atomic element distribution in TiNi films peeled off from SiO_2 substrate. The zero depth was the location of the $SiO_2/TiNi$ interface.

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low concentration. With increases of thickness, Ti content increases gradually and Ni content increases rapidly to approximately 50 at.% within approximately 25 nm. Both Si and C decrease quickly with depth and disappear at a depth of 15 nm. O elements can be detected as deep as 30 nm.

Fig. 8 shows high resolution Si 2p, Ni 2p and Ti 2p spectra evolution with depth. For Si 2p peak evolution shown in Fig. 8a, on the surface, the main peak at approximately 99.6 eV corresponds to Si-Si bonds, and the peak at approximately 103-104 eV is due to silicon oxides in the Si 2p spectrum. With increase of depth into TiNi films, Si-O peak disappears. There is slight shift and broadening of Si-Si bonds probably due to the formation of Ti-Si bond. Fig. 8b,c show the Ti and Ni 2p peak evolution with depth. Both Ti and Ni peak intensities increase with depth. Ni mainly exists in the metallic state, with broad satellite peaks probably due to the consequence of sputter-damaged crystallites. For Ti 2p spectra on surface, apart from metallic Ti peak, there is large amount of Ti-O peak. Beneath the surface, Ti-O bond reduces significantly, and Ti mainly exists as metallic state. The high intensity between the 2p 2/ 3 and 2p 1/2 peaks is due to the presence of shake-up satellite structures.

Fig. 7 shows the concentration changes of different elements into SiO_2 interface after TiNi is peeled off. On the surface, apart from large amount of C elements, Si and O elements are dominant, whereas traces of Ti can be found, and Ni content is below the detection limit of equipment. With increase of depth, no Ni can be observed to diffuse into SiO_2 layer. Titanium mainly exists in Ti–O bond, and its content decreases to zero within approximately 3 nm. Within approximately 6 nm, there is no carbon contamination found. Si/O remains at a stable ratio of 1:2 after 6 nm. Thus, inter-diffusion between SiO_2 substrate and TiNi film is very minimum, with a total interfusion zone thickness of approximately 20-30 nm.

In practice, TiNi films were often sputtered on glass substrate in order to obtain free standing films [2,3]. In fact that comes no surprise because SiO_2 is the main composition in glass. That proves, from a different angle, that TiNi does not adhere on SiO₂. Due to the existence of large amount of oxygen on the SiO_2 layer, titanium atoms arriving on the SiO₂ surface will be quickly oxidized, forming a thin layer of TiO_2 (see Ti^{4+} peak in Fig. 8c), significantly preventing the interdiffusion. However, the TiO₂ layer formed is fragile and brittle, which easily breaks during scratch test, thus the mechanical properties of the SiO₂/TiNi system are adversely affected. It was also reported that the adhesion of Ti-Ni to Si wafer could be improved if the Si wafer was pre-etched in buffered oxide etchant (BOF, $H_2O +$ $HNO_3 + HF$) prior to deposition [2]. One of the reasons



Fig. 8. Si 2p, Ni 2p and Ti 2p spectra evolution with depth into TiNi interface peeled from SiO_2 substrate, (a) Si 2p, (b) Ni 2p and (c) Ti 2p.

for this improvement is the removal of native surface oxide layer on Si wafer.

4. Conclusions

TiNi films were prepared on Si and Si/SiO_2 substrates through magnetron sputtering. In Si/TiNi system, there

existed significant inter-diffusion between Si substrate and TiNi film, and the interfacial diffusion zone was as thick as 120 nm (60 nm into Si and 60 nm into TiNi). Under the same conditions, with the SiO₂ sandwich layer, the interfacial diffusion zone thickness was reduced to only 30 nm (a four-fold reduction). XPS results confirmed that there was the formation of titanium silicides at the interface. The addition of SiO₂ sandwich layer did not alter the crystalline structures and shape memory properties of the shape memory thin film, but inversely affected the film adhesion on substrate: the lower critical load dropped from 180 mN in Si/TiNi system to only 50 mN in Si/SiO₂/TiNi system. (Therefore, application engineer needs to be mindful should the application call for high adhesion).

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