XPS characterization of surface and interfacial structure of sputtered TiNi films on Si substrate

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Abstract

TiNi films were prepared by co-sputtering TiNi and Ti targets. X-ray photoelectron spectroscopy (XPS) was employed to study surface chemistry of the films and interfacial structure of Si/TiNi system. Exposure of the TiNi film to the ambient atmosphere (23 °C and 80% relatively humidity) facilitated quick adsorption of oxygen and carbon on the surface. With time, carbon and oxygen content increased drastically at the surface, while oxygen diffused further into the layer. After a year, carbon content at the surface became as high as 65.57% and Ni dropped below the detection limit of XPS. Depth profiling revealed that significant inter-diffusion occurred between TiNi film and Si substrate with a layer of 90–100 nm. The detailed bond changes of different elements with depth were obtained using XPS and the formation of titanium silicides at the interface were identified.

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1. Introduction

TiNi based shape memory alloy (SMA) thin films offer a combination of novel properties, such as shape memory effect, pseudoelasticity, biocompatibility, good corrosion resistance and high damping capacity, which enable them to be widely used in numerous applications, especially in biomedical engineering and micro-electro-mechanical system (MEMS) [1–3]. Up to now, great effort has been made to produce TiNi based thin films using sputtering technique [4–11]. Vacuum deposited TiNi films generally show fine-grained structure and high surface reactivity and sensitivity. Therefore, it is important to understand the surface structure and its aging effect when exposed to ambient atmosphere. For TiNi films deposited on Si substrate, there are some reaction phases at TiNi/Si interface, which could affect the adhesion and shape memory properties, especially when the deposition is done at high temperatures (300–500 °C). The interfacial region formed between TiNi film and Si substrate can be complex, heterogeneous and metastable [12]. Since the TiNi film thickness required in MEMS is usually less than a few microns, a relatively thin reaction layer might have important effects on adhesion and shape memory properties. Recently, preparation of nano-layered TiNi film and fabrication of nano-scale shape memory structures or actuators are getting momentum. These actuators may be able to perform effective physical actuation (push, pull, move, place, etc.) at nano-scale with electron-beam or photon-beam local heating (instead of the conventional Joule heating methods). The information of the surface chemistry and interfacial structure is essential in designing of such actuators out of thin films. There were a few studies of TiNi/Si interfacial layer using transmission electron microscopy (TEM) [13,14], and very few on XPS study of surface and interfacial structures. In this investigation, TiNi films were prepared by co-sputtering of a TiNi target and a Ti target. After aging in ambient atmosphere up to 1 year, the surface chemistry of TiNi film was characterized using XPS. Interfacial chemical distribution between TiNi film and Si substrate was also studied.

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2. Experimental

Ti50Ni50 films of 4.5 μm thickness were prepared on 4-in. (1 0 0) silicon substrate heated to 723 K by co-sputtering a TiNi target (with atomic percentage of 50/50, rf 300 W) and a separate Ti target (dc 40 W) [11]. The substrate holder was rotated during deposition for uniformity. The base pressure of the deposition chamber was 1 × 10⁻⁷ Torr. The Si wafers were pre-sputtered with Ar plasma for 10 min using rf bias power (100 W) before deposition. During deposition, the argon pressure was 2.3 mTorr. The as-deposited samples were left in the ambient (23 °C and 80% relative humidity) for different periods up to 1 year. XPS analysis was performed on the TiNi film surface and TiNi/Si interface using a Kratos AXIS spectrometer with monochromatic Al Kα (1486.71 eV) X-ray radiation. The TiNi film was ductile and the freestanding films can be obtained after breaking the Si wafers (while the film remained unbroken). Both the “TiNi-side” and “Si-side” peeled off surfaces were immediately used to measure the elemental composition using XPS. The XPS survey spectra in the range of 0–1100 eV were recorded in 1 eV step for each sample, followed by high-resolution spectra over different element peaks in 0.1 eV steps, from which the detailed compositions were calculated. Curve fitting was performed after a Shirley background subtraction by a Lorenzian–Gaussian method. The pressure of the analysis chamber was lower than 10⁻⁷ Pa, which was increased to approximately 5 × 10⁻⁵ Pa during ion bombardment. For elemental depth profiling of the surface and interfacial structure, an ion gun (Kratos MacRoBeam) of 4 keV was used at a sputtering rate of 0.042 nm/s with Ar gas of high purity.

3. Results and discussions

3.1. Aging effect

XPS survey spectrum of TiNi film fresh from the deposition chamber (see Fig. 1, top spectrum) shows that the dominant signals are from Ti, Ni, C and O. Elemental surface composition analysis indicates that O content is about 36.92 at.%, Ti 31.03 at.%, Ni 18.54 at.% and C 13.51 at.% as listed in the first row of Table 1. Fig. 2 is the elemental depth profiling of the fresh sample. The amount of carbon and oxygen decreases significantly with depth and vanishes at 5 nm and 15 nm, respectively. It is possible that the reaction with residual gases in the spectrometer chamber or the ionic transport via impurities in the Ar gas causes the remained oxygen contents in films. Both titanium and nickel contents increase significantly with depth, as is expected. Ti-rich layer is observed in the first 6 nm, while a slightly Ni-rich layer is observed beneath this layer. The ratios between Ti and Ni maintain a stable value afterwards. As soon as the fresh TiNi film is exposed to the ambient, oxygen and carbon quickly adsorb on the surface because titanium has a high affinity for oxygen and carbon (chemisorb barrier energy or enthalpy for Ti and Ni to react with oxygen at surface are 241 kJ/mol and 956 kJ/mol, respectively [15]). The reduction of Ni on film surface appears to be the result of preferential oxidation of Ti, while the relatively high content of Ni in sub-layer is also due to this effect.

XPS survey spectrum on TiNi film exposed to ambient atmosphere for 3 months is shown in Fig. 1 (the middle spectrum). The dominant signals are from C, O and Ti, and the Ni peak becomes very weak (1.64 at.%). The elemental compositions thus obtained are also tabulated in Table 1. This indicates that the outermost layer of TiNi film is titanium oxide and carbon contamination layer. The oxide layer is about 50 nm thick and carbon diffusion layer

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Table 1

<table>
<thead>
<tr>
<th>Samples</th>
<th>Ti (at.%)</th>
<th>Ni (at.%)</th>
<th>O (at.%)</th>
<th>C (at.%)</th>
</tr>
</thead>
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<tr>
<td>Fresh</td>
<td>31.03</td>
<td>18.54</td>
<td>36.92</td>
<td>13.51</td>
</tr>
<tr>
<td>After 3 months</td>
<td>19.07</td>
<td>1.64</td>
<td>49.98</td>
<td>29.31</td>
</tr>
<tr>
<td>After 1 year</td>
<td>8.06</td>
<td>0</td>
<td>26.37</td>
<td>65.57</td>
</tr>
</tbody>
</table>

Fig. 1. XPS survey spectrum for TiNi film aged for different periods.

Fig. 2. XPS depth analysis showing the composition changes for fresh TiNi film.
is about 20 nm thick. Titanium and nickel increase significantly in the first 20 nm. Ti-rich layer is observed in the first 20 nm, while a slightly Ni-rich layer is observed beneath this layer.

In Fig. 1, the bottom spectrum is the survey spectrum of the film exposed to the air for 1 year. The C 1s peak is very strong and the Ni peaks disappear. High-resolution spectra analysis reveals that C content is as high as 65.57%, O content is about 26.37%, Ti content 8.06% and that of the Ni is below the detection limit of XPS as listed in Table 1. Fig. 3 shows the elemental depth profiling of the surface layer for sample aged for 1 year. Oxygen diffusion layer is about 60 nm thick and carbon layer 30 nm. Titanium and nickel increase significantly in the first 25 nm.

These findings show that the sputtered TiNi thin films are easily contaminated with carbon and oxygen in air. With exposure to atmosphere, carbon and oxygen increase drastically at the surface, and at the same time diffuse deep into the film. The increase is very fast at the beginning but slows down with time after long-time exposure.

3.2. Structural depth profile

Fig. 4 shows the evolution of Ti 2p peak with increase of depth for the film exposed to ambient atmosphere for 3 months. On the surface, Ti is mostly present as TiO₂ (Ti appears as Ti⁴⁺). Deconvolution results in eight different peaks corresponding to four chemical states from doublet consisting of Ti 2p₁/₂ and Ti 2p₃/₂: two strong Ti⁴⁺ peaks, i.e., 2p₁/₂ (Ti⁴⁺, 464.6 eV) and 2p₃/₂ oxide (Ti⁴⁺, 458.8 eV), two Ti³⁺ peaks (457 eV and 463.1 eV) and two Ti²⁺ peaks (455.3 eV and 461.7 eV), as well as two metallic Ti peaks (454.3 eV and 460.5 eV). The atomic percentages of Ti in Ti⁴⁺, Ti³⁺, Ti²⁺ and metallic Ti state are calculated and plotted in Fig. 5. Clearly, the amount of TiO₂ (Ti⁴⁺) decreases and metallic Ti increases significantly with depth. At the same time, both TiO (Ti⁴⁺) and Ti₂O₃ (Ti⁴⁺) firstly increase and then gradually decrease with depth. Ni 2p peak is relatively weak on surface, but this peak increases significantly with depth as shown in Fig. 6. Ni exists mainly in the metallic state with two distinct metallic Ni peaks at Ni 2p₁/₂ (852.6 eV) and Ni 2p₃/₂ (869.7 eV). The chemical state does not change with the depth.
High-resolution spectrum of O 1s binding energy region is shown in Fig. 7. There are several peaks, one is identified as strong O$^-$ peak (530.2 eV) and a weak O=C peak (532 eV). As shown in Fig. 7, the peaks decrease significantly at the first 1–2 nm. Further into the film, O$^-$ peak is dominant, which decreases gradually with the increase of depth. This indicates that oxygen elements diffuse and react with titanium to form titanium oxide deep into the film. Apart from O, there is also significant carbon chemi-adsorption as shown in Fig. 8. As a result of surface contamination due to hydrocarbon-rich atmosphere, the carbon adsorption reveals as a strong C=C bond (284.8 eV), a weak C=O peak (288.4 eV). With increasing depth, all these peaks decrease significantly and disappear.

High nickel content in TiNi based alloys often causes suspicion of its suitability for medical use. The presence of TiO$_2$ oxide layer on TiNi film prevents release of Ni element from surface, which is beneficial to corrosion resistance and bio-compatibility. However, it was reported that this passivation layer formed on the surface of bulk TiNi alloy was relatively fragile [15]. The mechanical properties of TiO$_2$ and TiNi are quite different, and this brittle and thin oxide layer may be destroyed during significant deformation or during complex interaction involving wear. Therefore, the stability and ductility of this native formed oxide layer has to be considered in proper implant design [16]. The optimized preparation and modification processes for this passivation layer, and prevention of surface layer degradation are crucial if the TiNi thin films are considered for medical applications [17].

### 3.3. Interfacial structure

We peeled off the TiNi films from the Si substrate and immediately measured the surface elemental composition, and the results are tabulated in Table 2. Large amount of O and C elements were found on both TiNi film interface and Si substrate due to the surface adsorption since the samples were exposed to ambient before the measurement. The depth profile of the atomic concentration evolution into TiNi interface is shown in Fig. 9. The surface region is characterized by C and O contamination (a few nanometer thick layer). Beneath it, there is a Si diffusion layer (about 30–40 nm thick). In TiNi film, the Ni content seems slightly higher than that of Ti, probably due to the preferential oxidation of Ti near surface and preferential sputtering of Ti during Ar ion beam bombardment. Results indicate that there is significant inter-diffusion of Si atoms into TiNi films, and silicon can be detected 40 nm beneath film surface. The diffusion of Si into

<table>
<thead>
<tr>
<th>Samples</th>
<th>Ti (at.%)</th>
<th>Ni (at.%)</th>
<th>O (at.%)</th>
<th>C (at.%)</th>
<th>Si (at.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiNi-side</td>
<td>13</td>
<td>4.98</td>
<td>32.28</td>
<td>30.55</td>
<td>19.28</td>
</tr>
<tr>
<td>Si-side</td>
<td>3.23</td>
<td>2.95</td>
<td>31.17</td>
<td>41.62</td>
<td>21.03</td>
</tr>
</tbody>
</table>

Table 2

Interfacial elemental compositions on freshly peeled, open surfaces.

Fig. 7. XPS depth analysis of O 1s peak on surface of TiNi film aged for 3 months.

Fig. 8. XPS depth analysis of C 1s peak on surface of TiNi film aged for 3 months.

Fig. 9. Atomic element distribution for TiNi interface peeled off from Si substrate.
At a relatively high deposition temperature of 450°C, significant inter-diffusion of Si, Ti and Ni could easily happen, and such a high temperature could also promote the formation of titanium or nickel silicides.

Fig. 10 shows high-resolution Si 2p, Ti 2p and Ni 2p spectra changing with depth into TiNi films. Fig. 10(a) shows the Si 2p peak evolution. On the surface (the first curve at the bottom), the peak component at about 99–100 eV corresponds to Si–Si bonds. There is also the contribution from silicon oxides (SiO$_2$) in the Si 2p spectrum at a binding energy of about 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. This is easily understood if account is taken into of the higher electronegativity of Si with respect to Ti or Ni (Si: 1.8, Ti: 1.5 and Ni: 1.8 [18]), thus a progressive shift to lower binding energy due to reactions among silicon and titanium elements would be expected. It was reported that the shift of Si 2p core levels at binding energies of −0.6 eV and −1.1 eV relative to the Si–Si bond corresponds to the formation of Ti–Si bond and Si in solution of Ti [19]. In brief, there are four distinct chemical environments 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 (or Ni)–Si compounds in the intermediate layer and (4) Si as a solution in TiNi films. The composition ratios of these components were calculated using deconvolution of Si spectrum and the results are shown in Fig. 11. At the surface, Si–O and Si–Si bonds are dominant. With the

![Figure 10 Si 2p, Ti 2p and Ni 2p spectra evolution with depth into TiNi interface peeled from Si substrate.](image1)

![Figure 11 The atomic percentages of different Si bonds diffused into TiNi interface.](image2)
increase of depth, Si–Ti bond increases. Further into TiNi film, Si mainly exists as a solution in TiNi. Fig. 10(b and c) shows Ti 2p 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 broad satellite peaks due to sputter-damaged crystallites [20]. No significant shift for Ni 2p peaks is observed. However, since the electronegativity values of Si with Ni are almost the same, thus even though there is nickel silicide formation, the chemical state may not be changed apparently. For Ti 2p spectra in Fig. 10(c), on the surface, apart from metallic Ti peak, there is some content of TiO2 peak due to oxygen contamination. Beneath surface, Ti mainly exists as metallic state. The presence of Ti–Si bonds for Ti 2p peak could be at about 454.8 eV [21], but overlap with TiO peak, thus it is difficult to calculate the percentage of Ti–Si bonds from Ti 2p peak evolution. In Refs. [13,14], different phases, such as NiS12, NiTiSi2, Ti4Ni3Si7 and Ti2NiSi, can be identified from TEM phases; however, from XPS analysis, it is difficult to identify the exact crystalline structures of these silicide phases.

Fig. 12 shows the concentration changes of Ti, Ni and Si elements into Si interface measured after the film is peeled off. Apart from surface contamination layer of about 10 nm, there is a TiNi diffusion layer of about 60 nm into the Si substrate. Both Ti and Ni contents firstly increase to a maximum (about 15 at.% at a depth of 10 nm), then gradually decrease. Fig. 13(a) shows the Si 2p peak into Si interface. On the surface, Si–Si and Si–O bonds are dominant. With increase of depth into Si substrate, there is an increase in left shoulder of Si–Si bond peak, indicating the formation of Ti–Si or Ni–Si component. While with further increase of depth, Si–O peak...
gradually decreases and Si–Ti (or Ni) peaks also decrease. Fig. 13b and c) shows the Ni 2p and the Ti 2p peaks evolution with depth. Both intensities of Ti and Ni peaks firstly increase with depth, then gradually decrease and finally disappear. Ni mainly exists in the metallic state and there is no significant change in peak position. For Ti 2p peak on the surface, apart from metallic Ti peak, there is large content of TiO2 peak due to oxygen contamination. Beneath the surface, Ti mainly exists in metallic state, and the high intensity between the 2p2/3 and 2p 1/2 peaks are attributed to small amount of Ti=O or the presence of Ti–Si bonds, but it is difficult to identify from Ti 2p peak evolution due to overlapping of different peaks.

In brief, there is significant inter-diffusion between Si substrate and TiNi films, and the total intermixing layer is about 90–100 nm. Also, XPS results confirm the formation of titanium silicides.

With aging in ambient atmosphere, carbon and oxygen contents increased drastically at the surface, and diffused into the Si substrate. There is also inter-diffusion layer between the Si substrate and TiNi films. These could pose challenges for preparation of nano-layered TiNi films or shape memory nano-structures: the films are so thin that surface oxide and oxygen diffusion into the substrate and inter-diffusion layer could have serious implications on the design of nano-layered thin film or shape memory nano-structures.

4. Conclusions

As soon as the TiNi film was exposed to the ambient atmosphere, oxygen and carbon quickly adsorbed on the surface. With aging in ambient atmosphere, carbon and oxygen contents increased drastically at the surface, and diffused into the Si substrate. After long-time aging, carbon content at the sample surface drastically increased (as high as 65.57 at.% after a year) and Ni dropped below the detection limit of XPS. XPS composition depth profiling revealed that the chemical bonding changes with depth and significant inter-diffusion occurred between TiNi film and Si substrate. Also, titanium silicides formed at the interface. These oxidation and oxygen/Si inter-diffusion could have serious implications on the design of nano-layered thin film or shape memory nano-structures.

References