NiTi thin films prepared by biased target ion beam deposition co-sputtering from elemental Ni and Ti targets

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NiTi thin films are fabricated using biased target ion beam deposition technique. By design, the technique operates over a broad range of processing pressures; enables control of adatom energies; facilitates low energy bombardment; and promotes uniformity and repeatability. Thus, the technique is advantageous for preparing smooth and dense ultrathin films. Typically NiTi shape memory alloy thin films are deposited using the magnetron-sputtering technique and alloy targets. In this work films are co-sputtered from pure Ti and pure Ni targets and the technique is contrast with magnetron co-sputtering. Approximately 100 nm thick NiTi thin films are prepared with Ni-rich (>50.5 at.% Ni), near equiatomic, and Ti-rich (<49.5 at.% Ni) compositions. Atomic force microscopy reveals that films are consistently ultra-smooth over the broad range of compositions. The current findings confirm that biased target ion beam deposition can facilitate the preparation of high quality ultrathin NiTi films. After heat-treatment, the films deposited exhibit B2 and B19′ crystal structures and thus possess potential for martensitic phase transformation, which is the prerequisite for functional shape memory behavior.

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1. Introduction

NiTi based thin films have been primarily fabricated by vacuum magnetron sputtering as the common form of physical vapor deposition[1]. The films that exhibit shape memory behavior have found applications as micro-grippers, micropumps, stents, and endoscopes, among other micro-scale applications[2–4]. Reports on conventional NiTi thin films—used in practical application—recommend fabricating using vacuum magnetron sputtering utilizing a NiTi alloy targets. There are inherent drawbacks: Ni sputters at a rate nearly three times than Ti; Ti can be lost to residual oxygen; the target composition may not be absolutely uniform[1]. Essential to fabrication of NiTi thin films with the shape memory effect are controlling chemical composition, having uniformity of composition over a large area and run to run, and ensuring quality[1,2]. To date, NiTi films exhibit shape memory behavior when thickness ranges from 0.5 to 2 μm[1]. Technological advancement for smaller scale applications requires the exploration of thinner films.

In this work, NiTi alloy film with thicknesses on the order of 100 nm are co-sputtered from separate Ni and Ti targets utilizing biased target ion beam deposition (BTIBD) technique. BTIBD allows differential biasing of each target BTIBD and combines ion beam deposition and sputtering deposition, and offers low-pressure operation[5–8]. A schematic of the BTIBD system is shown in Fig. 1. A low energy end-Hall (or closed-drift Hall) type ion source, typically lower than 25 eV, is introduced to the negative biased targets. A stable plasma must be maintained in the hollow cathode. The hollow cathode (HC) generates electrons and ejects electrons to the end-Hall ion source, rendering the plasma at the end-Hall constantly stable. A "wave" of ions carries the sputtered material to the substrate. Each target bias can be modulated differently by controlling the pulsed width and period. The capability of individual modulation can facilitate precisely controlling composition uniformity and stably maintaining deposition repeatability. Furthermore, bias target deposition allows control of medium energy Ar ions from the ion gun to impinge on the growing film and enables low ion energy bombardment with less impurities being sputtered. By design, on the other hand, the BTIBD technique enables controlling adatom energy (for high and low adatom energy process capabilities); decoupling adatom energy and deposition rate as well as target and substrate plasma; and directing the flux while providing low energy ion bombardment at low processing pressures 1 × 10−5 to 5 × 10−3 Torr[8]. Thus, the technique is advantageous for the fabrication of ultra thin and dense ultra smooth films.

Co-sputtering enabled the fabrication of NiTi thin films with Ni-rich (>50.5 at.% Ni); near equiatomic; and Ti-rich (<49.5 at.% Ni) compositions prepared using BTIBD. For preparing NiTi alloy thin films, the importance of controlling the alloy composition is reflected in Fig. 2. The ordinate axis is the temperature at which the thermal-induced martensitic transformation (TIMT) starts (referred to as M<sub>s</sub>); the TIMT being the foundation of shape memory behavior for practical application. Near-equimolar ranges from 49.5 to 50.5 at.% Ni based on Ref. [1]. The Ni-rich and Ti-rich regions are assigned outside that range. Note that,
within a very small range of compositions, 0.1 at% Ni change can facilitate a 10 °C change in \( M_s \). In this work, the BTIBD operating parameters are systematically adjusted for fine-tuning the alloy composition and deposition rate. We investigate very thin films (nearly 150 nm thick) compared to conventional shape memory NiTi thin films. We report findings of morphological observations in transmission electron microscopy (TEM), composition measurements in inductively coupled plasma atomic emission spectroscopy (ICP-AES), and surface roughness measurements from atomic force microscopy. The BTIBD films are compared to a control group of films deposited by the conventional magnetron sputtering in vacuum. Without optimizing the operating parameters, BTIB yields high quality NiTi films of very thin dimensions.

Previous works on sputtered thin films, with similar thickness to our films (100–200 nm), have also observed coexisted B2 and B19′ phases after heat treatment for crystallization and the film exhibits shape memory behavior. With in-situ crystallization in TEM, B2 at high temperature was identified in sputtered NiTi film with 200 nm thickness, and after crystallization, B2 and B19′ co-exist. Upon heating to 60 °C, the reverse transformation from B19′ to B2 occurs with only B2 phase remaining [9,10]. In [11], after the as-deposited sputtered NiTi film with 105 nm thickness was post-annealed, the coexistence of B2 and B19′ is observed, and the phase transformation was confirmed by measuring the residual stress as the temperature changes. Thicker sputtered NiTi film (~1 μm thick) also had the coexistence of B2, B19′ after annealing at 600 °C for 1 h and cooling to room temperature, and the heat flow versus temperature plot from differential scanning calorimetry test revealed the occurrence of phase transformation [12]. In this work, the coexistence of B2 and B19′, after heat-treatment of as-deposited NiTi film, confirms the potential for phase transformation, and thus shape memory behavior. Heat-treatment is able to render the deposited films to be crystalline and was utilized to crystallize BTIBD NiTi films. Grain morphology, and B2, B19′ crystal structures, after heat-treatment, are demonstrated, with potential for martensitic phase transformation.

2. Experimental details

Film depositions were performed in the Nanofabrication Laboratory of Materials Research Institute, the Penn State University. The BTIBD films were deposited using the Biased Target Ion Beam Deposition system developed by 4 Wave Incorporated. Magnetron co-sputtered films were deposited using a Kurt Lesker CMS-18 Multi Target Sputter system. Calibrating operational parameters for both systems was conducted to maintain stable plasma, minimize the materials sputtered from the vacuum chamber, provide sufficient energy to generate electrons, and keep enough current in target for high deposition rate. The BTIBD operational pressure parameters were then set to 6.5 × 10−4 Torr, and Ar flow rate in ion source and HC were 60 and 10 sccm, respectively; the base pressure was 1.7 × 10−7 Torr. For magnetron, the operational pressure parameters were then set at the value 3.65 × 10−3 Torr, and the Ar flow was set at 19.4 sccm. The BTIBD target was pre-cleaned for 600 s and then the pre-cleaning on substrate was conducted with ion source on for 600 s. The base pressure was 1.3 × 10−7 Torr. Prior to actual magnetron sputter deposition, a seasoning procedure of the targets was conducted, with the same deposition parameter as the actual deposition set for 120 s. In both cases, deposition is at room temperature and the Ti input is constant and the Ni input is varied in order to control composition. Also, the substrate is rotated in order to achieve compositional uniformity and the speed is 20 rpm.

Table 1 shows the power specifications used to sputter films using the BTIBD and conventional magnetron systems. During actual deposition, the Ti target and Ni target were both biased with −805 V. The width and period of the pulse, on the other hand, were allocated separately. The Ti was set to zero pulse so the pulse width and pulse period are equal (i.e. 100/100 = 1). The pulsed period for Ni is also set to 100 s. However, the Ni pulsed width is systematically varied. For magnetron co-sputtering, the titanium target was powered with 200 W in order to achieve maximum deposition rate. The nickel target power could be varied up to 300 W of RF power: here it was varied from 75 to 155 W.

We utilize a DuraSiN chip, manufactured by Protochips, Inc., that is 2.65 mm in diameter and made up of two materials as shown in Fig. 3(a). An amorphous silicon nitride (SiN) membrane (30 nm in thickness) is atop a silicon substrate (300 micron thick). The central part of the Si is etched thoroughly so that the corresponding area of the SiN membrane is exposed. Thus, the deposited NiTi film plus SiN membrane is electron-transparent. The configuration circumvents conventional TEM sample preparation, which can obscure image interpretation. The approach is adopted from Refs. [9] and [10]. Furthermore, for this work, the DuraSiN chip enabled multiple microscopy techniques conducted on one specimen as shown in Fig. 3(b). The crystal structure
and microstructure of NiTi film were analyzed in a TEM (JEOL EM-2010F operating at 200 kV). Energy-filtering TEM (EFTEM) thickness map was acquired by using JEOL 2010 LaB₆ TEM at 200 kV combined with an energy-filter. An atomic force microscope (AFM by Bruker Icon) with contact mode was utilized for measuring surface morphology of the films at room temperature. The AFM data was collected on a Dimension Icon instrument (Bruker Nano Surface Santa Barbara, CA) in PeakForce tapping mode using SCANASYST-AIR probes (Bruker AFM Probes Camarillo, CA). SCANASYST-AIR probes consist of a SiN cantilever with Si probe, 5 nm nominal tip radius, and 0.4 N/m nominal spring constant. Images were collected at 1 micron by 1 micron with PeakForce set points in the 0.5–1.0 nN range and scan speeds of 0.25–0.75 Hz. Offline analysis was done with Nanoscope Analysis version 1.40 (Bruker Nano Surface Santa Barbara, CA). All displayed images had the Z color scale set to a range of −6 nm to 6 nm for comparison purposes.

Two other types of substrates were used in each deposition: Kapton tapes for composition measurements and a photoresist-masked silicon piece. The composition of NiTi film was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES). The detection limit was Ti 0.002 g/mL and Ni 0.006 g/mL due to the nature of destructively dissolving the film; ICP-AES required the Kapton tape as the substrate for NiTi films. The tape is insoluble to the etchant of the dissolving film. The thickness of the films was measured in stylus profilometer (P16+ KLA-Tencor Corporation). The measurement technique involved using a step height generated in photoresist-masked silicon pieces, the other kind of substrate (30 mm × 30 mm in area, 500 μm in thickness) used in all the depositions. After LOR A5 and SPR 3012 photoresist on silicon piece was routinely spun and exposed, the NiTi films, in one deposition, were on the patterned silicon piece. By stripping the removable resist on silicon piece, a well-defined steps height of NiTi films was generated, and ready to measure.

The films on DuraSiN chip substrate underwent heat-treatment in Rapid Thermal Annealing (RTA, Allwin21, Corp.). Table 2 shows the heat-treatment condition and results of heated thin films. Three Ni concentrations, 28.0 at.%, 49.7 at.%, and 51.7 at.%, were chosen from Ni-poor (or Ti-rich), near-equiatomic, and Ni-rich regions for heat-treatment in order to obtain the grain morphology and crystal structure in each region because NiTi is highly composition-sensitive. The heat-treatment process is in the second column. First, the treatment consisted of increasing to target temperature and then maintaining for 1 min. The temperature was raised to a second higher temperature which was maintained for 5 min. The heat treatment for the Ni-rich alloy is the exception; with third and fourth heating and hold times. This additional heat treatment facilitated crystallization, as the Ni-rich film was amorphous after the first two heats. In every case, the specimen was finally allowed to naturally cool down to room temperature. The heated thin films were examined in TEM bright field mode for grain morphology and diffraction mode for crystal structure.

### 3. Results

A TEM image of Ni-rich Ni₆₀₂₉₂Ti₃₉.₈ (at.%) thin film prepared using BTIBD is shown in Fig. 4. The inset diffraction patterns show diffuse rings that indicate that the sputtered film is amorphous. It is well known that as deposited NiTi films are amorphous [9,10]. The image is gray and featureless similar to previously reported observations for amorphous NiTi thin films [9,10]. The surface topography is measured using AFM. Three characteristic roughness measures are peak-to-valley roughness (Zₚᵥ), average roughness (Rₐ), and root mean squared (RMS). Measurements are plotted as a function of the Ni concentration in the NiTi thin film in Fig. 5. The average roughness and RMS are very close in Fig. 5. There is a miniscule increase with increasing Ni content. The peak-to-valley roughness also displays a miniscule variation though the magnitude is more substantial relative to the other measures. Fig. 6 shows TEM and AFM analysis for the Ni₆₀₂₉₂Ti₃₉.₈ (at.%) thin film at a higher magnification. The AFM image is shown in Fig. 6(b). The Zₚᵥ height was measured along different cross-sections as shown in Fig. 6(c). Along each section, the average Zₚᵥ is less than 0.6 nm. Similarly the Ti-rich Ti₇₉₂Ni₂₀₈ and near-equiatomic...
Ti51.4Ni48.6 thin films synthesized in BTIBD are amorphous and uniformly ultra-smooth, with the $Z_{\text{max}} < 0.6 \text{ nm}$.

Fig. 7 shows the TEM and AFM analysis for a Ni-rich Ni$_{55.7}$Ti$_{44.3}$ (at.%) magnetron sputtered thin film. The diffraction pattern, as well as the featureless surface, corroborates that the film is amorphous. Along cross-sections of the AFM topography in Fig. 7(b), the $Z_{\text{max}}$ height is much larger than those for the BTIBD film in Fig. 6. Roughness measurements as a function of magnetron film composition are also included in Fig. 5. The roughness measurements of magnetron film are highly composition-dependent relative to BTIBD. When the magnetron film is viewed at a higher magnification in the TEM, Fig. 8(a) exhibits striking features. The EFTEM of the region corresponding to Fig. 8(b) provides the local normalized thickness ($t/\lambda$) map via the log-ratio method [14,15]. The $t/\lambda$ map for Fig. 8(b) is demonstrated in Fig. 8(c). The dark area in Fig. 8(a) allows less beam through to be recorded so that in thickness $t$ is the absolute thicknesses and $\lambda$ is the inelastic mean free path. Since the film was deposited in a rotated condition and thus a uniform composition, $\lambda$ is a constant, and $t/\lambda$ gives the profile of thickness distribution. The thickness profile of one selected area, marked as a dash rectangle in Fig. 8(b), is shown in Fig. 8(c). The results imply that the densest material is in the island areas. Relative to the island areas, we consider the channels unfilled. Since the BTIBD NiTi films with the order of 100 nm thickness were deposited at room temperature and did not show any crystallographic phase, evidenced by the diffuse ring in the diffraction pattern of Figs. 4, 6, and 7 in the manuscript, the films were subjected to heat treatments in order to crystallize the films.

Table 2

<table>
<thead>
<tr>
<th>Composition (at.% Ni)</th>
<th>Heat-treatment</th>
<th>Phases</th>
</tr>
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<tbody>
<tr>
<td>28.0</td>
<td>450 °C for 1 min, then 500 °C for 5 min</td>
<td>B2, B19, Ti$_5$Ni</td>
</tr>
<tr>
<td>49.7</td>
<td>450 °C for 1 min, then 500 °C for 5 min</td>
<td>B19, Ti$_5$Ni</td>
</tr>
<tr>
<td>51.7</td>
<td>450 °C for 1 min, then 500 °C for 5 min</td>
<td>B19, Ti$_5$Ni</td>
</tr>
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Fig. 5. Roughness measurements ($Z_{\text{max}} =$ peak-to-valley; $R_a =$ average roughness; and RMS = root mean squared) as a function of the at.% Ni concentration in NiTi for films fabricated using biased target ion beam deposited (BTIBD) and magnetron sputtering (MS).

Fig. 4. TEM image showing BTIBD Ni-rich NiTi thin film in the as-deposited state at room temperature. Inset diffraction pattern which does not reflect crystallinity.

Fig. 6. (a) Image of the BTIBD NiTi ultra-smooth Ni-rich Ni$_{51}$Ti$_{49}$ thin film at 10,000×. (b) Magnified view (25,000×) showing BTIBD Ni-rich Ni$_{51}$Ti$_{49}$ thin film RHEED pattern. (c) Map showing the film is crystalline with different grain sizes. The rationale for observed structural heterogeneities were consistently observed. Moreover, the surface roughness of magnetron sputtered films is composition

4. Discussion

BTIBD and magnetron sputtered NiTi thin film growth can be classified in the Volmer–Weber (VW) growth model, which is common when metals are deposited on SiO$_2$ and grown near room temperature [16]. Physical vapor deposition (PVD) involves the condensation of vaporized component of materials on the substrate surface under vacuum. The stages of PVD thin film growth are nucleation, growth, and coalescence [16]. The deposition of thin solid film commences with a nucleation stage and clusters of atoms form islands on the substrate surface. A growth stage follows as deposition continues, in which islands take on impinging atoms and grow as nuclei until they reach a sub-critical size. A coalescence stage follows and in order to reduce surface area, small islands coalesce and agglomeration facilitates the formation of bigger islands until a continuous film is deposited.

Agglomeration is related to surface mobility of the adsorbed species and increasing adatom’s surface mobility facilitates the agglomeration. For the current magnetron sputtered ultrathin films, rather than the islands coalescing to form a continuous film, unfilled channels separate a network of islands. The unfilled channels appear white in TEM images, which are not obvious for the ultrathin BTIBD NiTi films (compare Figs. 3(d) and 4(d)). Hytonen et al. specify that two advantages of BTIBD technique are control of adatom energies and a large range of process pressures [8]. The findings in this work confirm that the BTIBD technique enables adatom surface mobility (and thus mass transfer) of co-sputtered Ni and Ti such that coalescence during deposition of NiTi films is enhanced. The authors note that they did not optimize either the BTIBD or the magnetron deposition parameters to minimize or eliminate unfilled channels. When using magnetron sputtering, the micro-structural heterogeneities were consistently observed. Moreover, the surface roughness of magnetron sputtered films is composition
dependent and assuming that the channels correlate to surface roughness, the results clearly suggest that BTIBD inherently enhances coalescence. Thus, BTIBD is advantageous for the deposition of different compositions of ultrathin NiTi films. The underlying mechanism of shape memory behavior is martensitic transformation, the transformation between two crystallographic phase, B2 phase and B19′ phase, in case of NiTi based SMAs. The amorphous films were subjected to heat treatment in order to crystallize the films.

As in Fig. 2, transformation temperature of Ni49.7Ti50.3 is about 320 K which is higher than room temperature (294 K), probably leading to complete transformation of austenite to martensite. This complete transformation explains that only B19′ phase exists at room temperature in Ni49.7Ti50.3. Also based on Fig. 2, the Ni_{28.0}Ti_{72.0} film will have a similar transformation temperature to Ni_{49.7}Ti_{50.3}, and thus should have only B19′ phase at room temperature. However, both B2 and B19′ phases are present in the Ni_{28.0}Ti_{72.0} film. The coexistence can be explained by the grain size effect on transformation temperature reported in [17,18]. The smaller grains in the Ni_{28.0}Ti_{72.0} film (Fig. 9(a)), compared to the Ni_{28.0}Ti_{72.0} film (Fig. 9(b)), will facilitate an increase in the transformation barrier. As more driving force from thermomechanical energy is required to initiate the transformation, the transformation temperature will decrease to provide the additional undercooling. With the lowered transformation temperature, the Ni_{28.0}Ti_{72.0} film would have incomplete transformation at room temperature. The preceding argument cannot explain the coexistence of B2 and B19′ phases in the Ni_{51.7}Ti_{48.3} alloy film based on Ni-rich composition. The coexisting phases are attributed to the additional higher temperature heat treatments and associated stress, which may facilitate the diffuse nature of the rings.

5. Conclusions

In this work, we demonstrate the potential of co-sputtering Ni and Ti using biased target ion beam deposition (BTIBD) to deposit NiTi films that are a few 100 nm thickness. BTIBD is capable of producing a range of composition and microstructure in the NiTi film including Ni-rich (>51.0 at.% Ni); near equiatomic; and Ti-rich (<49.0 at.% Ni). For both BTIBD and magnetron sputtering, operational parameters were adjusted with the aim of controlling composition and deposition rate. Adjusting some magnetron process parameters can possibly improve film quality: biasing the substrate and varying substrate and/or target temperatures to affect adatom mobility [19]. However, our work exemplifies that BTIBD readily enables alloy control and low energy bombardment, and consistently yields high quality ultrathin NiTi films.
different alloy compositions that are uniform at the nanoscale without additional adjustments on operating parameter.

Crystallographic phases, B2 phase and B19' phase, were obtained from the as-deposited NiTi films after heat-treatment. These two phases are prerequisite for martensitic phase transformation which is the underlying mechanism of shape memory behavior in NiTi. The existence of B2 and B19' phases exhibits potential for phase transformation, and thus shape memory behavior of the 100 nm BTIBD NiTi thin film. For conventional NiTi thin film fabrication, via magnetron sputtering, size effects are expected when the film thickness is below 0.5 μm and/or the grain size is between 50 and 100 nm [18,20]. The higher quality BTIBD films will enable unparalleled insight into size and composition effects on NiTi film shape memory capacity.

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