I. INTRODUCTION

Shape memory alloy thin films is of great interest because of the highest output work density (about $10^7$ J m$^{-2}$) with high actuation stress (over 500 MPa) and large recoverable strains (up to 10%) among the smart materials families (electromagnetic, thermos-pneumatic, electrostatic, etc.). Advancing miniaturization to the nanoelectromechanical systems requires the fabrication of nanoscale shape memory alloys and the characterization of properties at the nanoscale. Deposition of high quality nanoscale thickness films is an essential step. Till date, sputtering is the most commonly used film technology to deposit shape memory alloy thin films of micrometer thicknesses. When films of nanoscale thickness were deposited and tested by the stress-temperature method and by resistivity-temperature method, a critical thickness (~100 nm) became apparent, below which there was no shape memory response. The shape memory response was prohibited most likely due to, in addition to the constraint from free surface and substrate–film interface, difficulty in the repeated, precise control of composition, and in atomically tailoring the film growth. Biased target ion beam deposition (BTIBD), a recently developed film technology, is well-suited for the atomically engineered thin films given its wide range of processing pressures, ability to control adatom energy, and remarkable repeatability and uniformity.

In our previous work, we demonstrated that BTIBD is capable of producing nanoscale thickness NiTi thin films with the following features: a broad range of compositions, ultrasmooth surface, minimal diffusional interface, and transformable crystal phases. The thin films produced by BTIBD maintain high quality even on the order of a few tens of Angstroms, compelling quality at the very thin level is challenging for magnetron sputtering, which is more suitable to deposit thicker films. Moreover, high uniformity in thickness, less “overspill” contamination, and decreased mixing in between interlayer of multilayers have been recently reported for BTIBD films. The configuration of independent ion beam sources and sputtering targets, ultrahigh pressure, as well as the working principle, was explained in our previous work.

Crystallization heat treatment is necessary to produce the B2 atomic crystal structure for the crystallographically reversible martensitic phase transformation that results in shape memory behavior. As-deposited NiTi thin films are typically amorphous and do not exhibit shape memory behavior. Crystallization of the as-deposited films is essential to tailor the microstructure such as grain size, and to avoid unwanted microstructures such as deformation-induced defects. Crystallization is typically accomplished by postdeposition annealing. Till date, there is only one systematic study of magnetron sputtered films (~200 nm thick) during postannealing. Furthermore, in bulk materials, a critical grain size of 50 nm has been reported to significantly increase the energy barrier of martensitic transformation, which suppressed shape memory behaviors. Our recent work on BTIBD films reported preliminary microstructure characterization, showing grain sizes nearly three times that critical size in film thickness on the order of 100 nm. Understanding the crystallization of high-quality nanoscale thickness films fabricated using BTIBD will...
provide a basis to tailor the microstructure evolution for furthering shape memory functionality into the nanoscale.

This work investigates the crystallization and the microstructural development of nanoscale thickness NiTi thin films fabricated by BTIBD. In situ transmission electron microscopy (TEM) is used to monitor the development of grain morphology and crystal structure. The in situ monitoring is augmented by ex situ postdeposition heating on as-deposited films in the composition range from Ti-rich to Ni-rich. The surface morphology is examined using an atomic force microscope (AFM) in order to expound on the microstructure characterization. The local film density is examined using scanning transmission electron microscopy (STEM) and energy dispersive x-ray spectroscopy (EDS). The results of films fabricated using BTIBD are compared with those for films fabricated using magnetron sputtering.

II. EXPERIMENT

NiTi alloy thin films were deposited using a magnetron sputtering system (Combinatorial Materials Science Series, Kurt J. Lesker Company) and a BTIBD system (4Wave Cluster Sputter, 4Wave, Inc.), both of which are located at the Nanofabrication Laboratory of The Pennsylvania State University. The deposition rate was calibrated by measuring the thickness achieved within a given time in order to control the film thickness by adjusting the deposition time. The film thickness was measured using a profilometer (P-16+, KLA-Tencor Corporation) with a fraction of the thin film in a step-substrate-step configuration. The thin film composition was controlled based on the power ratio. To correlate the power ratio with the binary elemental concentration, the power applied to the Ti target was incrementally varied while keeping the power unchanged on the Ni target for calibrating. In each deposition, NiTi thin films deposited on Kapton tapes (10 mm x 5 mm area) was used for composition measurements in an inductively coupled plasma atomic emission spectrometry (5300 DV, PerkinElmer Inc.) with an accuracy down to 0.5 at. % Ni. Note due to destructive nature of dissolving thin films, Kapton tapes, which were not dissolvable to the etchant of dissolving thin films, were chosen for composition measurement. The current BTIBD system is configured with three targets, and for each target, individual control on the power of each target can be achieved. Potentially, alloy films with up to three elements or multilayers thin film can be deposited. High temperature stage was not equipped in the current BTIBD system. However, irradiation by the ion-beam source can raise the temperature of substrate prior to the deposition, and the resulting temperature can be up to 120 °C. The principles of the film deposition techniques and the detailed deposition parameters can be found in our previous work.21,26

Electron transparent SiN chips were used as the substrates for direct microstructure characterization. Each of the SiN chips purchased from Ted Pella, Inc., consisted of a SiN membrane (~30 nm thick) on top of silicon frame (~50 μm thick), which had a hollow center (250 by 250 μm²) to expose the SiN membrane. The SiN membrane was amorphous and underwent a precleaning with ions for 600 s prior to the actual deposition. The chips were circular with 3 mm diameters in order to precisely fit into the circular mounting hole of the TEM holder. Using a SiN chip enables the real time monitoring of microstructural development associated with crystallization. The crystal structure and grain morphology of the thin films were characterized using a TEM (JEOL 2010, JEOL, Inc.) at the 200 kV accelerating voltage. The surface topography was examined using an AFM (Dimension Icon, Bruker Corporation) with the scanning rate of 1 Hz and the scanning size equal to 1 x 1 μm.

For crystallization, the as-deposited NiTi thin films were heat-treated either in situ (using the TEM heating holder) or ex situ (using postdeposition rapid thermal annealing-RTA, Allwin21, Corp.). The heat treatment and sample details are shown in Table I. The samples are grouped according to the Ni content: Ni-poor/Ti-rich (<49.5 at. % Ni); near equiatomic NiTi (in between 49.5 and 50.5 at. % Ni); and Ni-rich (>50.5 at. % Ni) film composition.22 Note the variation in composition of BTIBD films is less than that in sputtered film, indicating the uniformity and repeatability of BTIBD in composition control. The heating parameters were chosen based on the reported parameters1,35 and the attempted parameters in our own tests.22 The parameters were maintained for each sample until the sample had completed the crystallization. Note that the time and temperatures differed due to samples having

<table>
<thead>
<tr>
<th>Synthesis technique</th>
<th>Heat-treatment apparatus</th>
<th>Composition (at. % Ni)</th>
<th>Thickness (nm)</th>
<th>Heat-treatment temperature (°C) and time (min)</th>
<th>Figures showing micrographs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sputtering</td>
<td>TEM</td>
<td>42.4 ± 1.8</td>
<td>30</td>
<td>490 °C 50 min, then 500 °C–17 min, to 520 °C–15 min, to 550 °C–23 min, to 610 °C–29 min, to 650 °C–28 min, to 700 °C–10 min</td>
<td>Figs. 2(a) and 2(d)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>52.1 ± 0.5</td>
<td>60</td>
<td>490 °C 5 min, then 500 °C 32 min</td>
<td>Figs. 2(b) and 2(e)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>55.5 ± 1.0</td>
<td>30</td>
<td>450 °C 40 min</td>
<td>Figs. 3(a)–1(i)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>120</td>
<td>500 °C 30 min</td>
<td>Figs. 2(c) and 2(f)</td>
</tr>
<tr>
<td>BTIBD</td>
<td>RTA</td>
<td>49.7 ± 0.2</td>
<td>99.7</td>
<td>450 °C 1 min, then 500 °C for 5 min</td>
<td>Figs. 3(a) and 3(e)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>51.7 ± 0.5</td>
<td>101.3</td>
<td>450 °C 1 min, 500 °C 5 min, 500 °C 3 min, and then 515 °C for 3 min</td>
<td>Figs. 3(b) and 3(f)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>54.5 ± 0.2</td>
<td>105.3</td>
<td>450 °C for 1 min, then 500 °C for 5 min</td>
<td>Figs. 3(c) and 3(g)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>62.8 ± 0.5</td>
<td>120.2</td>
<td>450 °C for 1 min, then 500 °C for 5 min</td>
<td>Figs. 3(d) and 3(h)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>60.2 ± 0.4</td>
<td>114.5</td>
<td>450 °C for 10 min, then 500 °C for 50 min</td>
<td>Figs. 1(j)–1(r)</td>
</tr>
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</table>

different compositions as well as synthesis methods. A TEM (JEOL EM–2010F, JEOL, Inc.) outfitted with a solid-state x-ray detector (EDAX, division of AMETEK) was operated at the accelerating voltage 200 kV to acquire the STEM images and EDS data. The EDS analysis was conducted in STEM mode, and the probe size for STEM imaging and EDS analysis was typically below 1 nm and here set as 0.7 nm.

III. RESULTS

TEM images in Fig. 1 show the initiation and evolution of crystallization during in situ heat treatment of films that were fabricated using magnetron sputtering [Figs. 1(a)–1(i)] and using BTIBD [Figs. 1(j)–1(r)]. The composition of the BTIBD film and the sputtered film is Ni-rich, in general.
In the sputtered film, diffraction patterns obtained before heating in Fig. 1(a) show diffuse rings that indicate the as-deposited film is amorphous. During heating, the appearance of sharp and clear rings in Fig. 1(d) indicates the formation of crystals. After heating, well-defined rings become obvious in Fig. 1(g); indexing confirms the crystal structure is B2. As for microstructure, the TEM image in Fig. 1(b) appears featureless, and the higher magnification image in Fig. 1(c) reveals a network of large gray, circular regions surrounded by white boundaries. Our previous work defined the gray regions as “islands” and the white boundaries as “channels.”

Crystals appear during heating, marked with a solid arrow in Fig. 1(e). In Fig. 1(f), crystals span channels and seem to merge islands as pointed out by open arrows. The crystals are about 8 nm in diameter. After heating, it is evident in Figs. 1(h) and 1(i) that the crystal size increases modestly to ~10 nm in diameter. Note that white boundaries are faintly visible during and after heating.

The diffraction pattern in Fig. 1(j) is for the film fabricated using BTIBD before heating and the diffuse rings within the pattern indicate an amorphous film. The heat treatment (450°C, 10 min) for sputtered film in Figs. 1(d)–1(f) is the same as that for BTIBD film in Figs. 1(m)–1(o). For BTIBD films, however, diffraction spots are apparent in the diffuse rings in Fig. 1(m). After heating, discrete diffraction spots exist in Fig. 1(p). The spots belong to the diffraction ring pattern for the B2 crystal structure. The appearance of discrete diffraction spots underscores that larger crystals, which have crystallographic planes of the same orientation, can form for BTIBD films. The BTIBD film is featureless in both low [Fig. 1(k)] and high [Fig. 1(l)] magnification TEM images, in stark contrast to the sputtered film. Heat-treatment produces giant, compared to sputtered film [see Fig. 1(e)], crystals that are more than 100 nm in diameter as circled in yellow in Fig. 1(n). Also, small crystals circled in yellow in Fig. 1(o) have ~5 nm in diameter. Upon visual inspection for a qualitative comparison with Fig. 1(f), the amount of crystals increases for the BTIBD film. After heating, in Figs. 1(q) and 1(r), the amount of giant crystals, with a size larger than 200 nm, noticeably increases; one example crystal is circled in yellow in Fig. 1(q). In general, the crystal sizes are on the order of 50 nm.

The microstructures for the ex situ (i.e., postdeposition RTA) heat-treatment of Ni-poor (42.2 at. % Ni) and Ni-rich (52 at. % Ni and 55.7 at. % Ni) sputtered films (Fig. 2) are contrasted with BTIBD films (Fig. 3) having near equiatomic (49.7 at. % Ni) and Ni-rich (51.7 at. % Ni, 54.6 at. % Ni, and 62.5 at. % Ni) composition. As for all the sputtered films in the as-deposited condition in Figs. 2(a)–2(c), a network of channels surround island regions. The findings illustrate that channels and islands are ubiquitous for magnetron sputtered films, which we attribute to limited adatom mobility playing an important role in the nanoscale thickness film deposition. The images after heating in Figs. 2(d)–2(f) reveal that the merging of islands prevails, marked with open arrows. In Figs. 3(a)–3(d), all the as-deposited BTIBD films are featureless in comparison with sputtered films. After heat-treatment, crystals are formed in Figs. 3(e)–3(h). On average, the size of crystals in the BTIBD films (>50 nm) is larger than that (10–20 nm) in the sputtered films. Among the BTIBD films, the near equiatomic composition (49.7 at. % Ni) has the largest crystals, ~100 nm as circled in Fig. 3(e), and the crystal size remains roughly 60 nm in slightly Ni-rich (51.7 at. % Ni) film.

For the Ni-rich films fabricated using BTIBD, comparing microstructural development after heating in Figs. 1 and 3 enables assessment of the influence of the heat treatment method. The results for the in situ TEM heat treatment of the film with 60.2 at. % Ni concentration are shown in Figs. 1(q) and 1(r). The results for the ex situ RTA of films with 54.6 and 62.5 at. % Ni concentrations are shown in Figs. 3(g) and 3(h). The microstructures exhibit similar crystal sizes on the order of 10 nm in diameter, and thus, the heat treatment apparatus appears inconsequential to assessing the BTIBD technique. Consequently, we believe that the differential heat treatment methods in Fig. 1 (in situ) and Fig. 3 (ex situ) do not detract from the comparative analysis in the preceding paragraphs.

![Fig. 2.](Color online) TEM bright field micrographs before (a)–(c) and after (d)–(f) in situ TEM heating of sputtered NiTi films. The open arrows in (d)–(f) mark the original location of channels prior to merging of the islands. Note that the 55.7 at. % Ni has the same composition but larger thickness compared to the sputtered film in Fig. 1.)
IV. DISCUSSION

Examining the surface topography of the as-deposited BTIBD films versus sputtered films provides the basis for contrasting crystallization morphologies that arise during and after heat-treatment. Figure 4 shows the surface topography, prior to heat-treatment, for sputtered films with Ni-poor (42.2 at. % Ni) and Ni-rich (55.7 at. % Ni) compositions (top row) versus BTIBD films with near equiatomic (49.7 at. % Ni) and Ni-rich (60.2 at. % Ni) compositions (lower row). In sputtered films, large amounts of islands appear as rod-shaped columns,\textsuperscript{21} as pointed out by the arrow in Fig. 4(a). The lower height regions are considered as the channels.\textsuperscript{21} The Ti-rich film (42.2 at. % Ni) in Fig. 4(a) has higher columns (and hence the darker contour on the color scale) than the Ni-poor film (55.7 at. % Ni).
Ni-rich (55.7 at. % Ni) film in Fig. 4(b). The columnar-channel microstructure is prevalent for sputtered films and will be referred to as columnar-void, which is consistent with fundamental descriptions. In BTIBD films, tiny height differences are apparent throughout the film plane for the near equiatomic [49.7 at. % Ni in Fig. 4(c)] and Ni-rich [60.2 at. % Ni in Fig. 4(d)]. Both BTIBD films exhibit unsubstantial height variations, compared to the films fabricated using magnetron sputtering. The differential as-deposited film morphology inherent to each technique likely influence the energy required for crystallization.

The columnar-void microstructure can be attributed to limited adatom mobility when magnetron sputtering is used. The limited adatom mobility facilitates shadowing the unoccupied surface sites from the depositing atoms, referred to as the self-shadowing effect. Recent microstructure studies on thicker (0.5–1 μm) NiTi alloy thin films fabricated using substrate-bias assisted magnetron sputtering displayed reduced roughness. It was suggested that increasing adatom mobility can greatly reduce the columnar-void morphology.

In order to elucidate the material elements and their relative amounts within column versus void regions, EDS analysis was conducted on the as-deposited sputtered film as shown in Fig. 5. The STEM image in Fig. 5(a) shows that the rod-shaped columns are bright, and the voids are dark. Although the profile view of columns in Fig. 5(a) resembles crystallographic grains, the structure is amorphous [see Fig. 1(a)]. In Fig. 5(b), the EDS analysis on one rod-shaped column at site A and on one void at site B provide a qualitative means to assess the total volume of materials excited by the STEM probe with the same collection time 60 s. The peak positions of each element in site A are consistent with those in site B, indicating that there is no difference in the type of material elements. The counts, i.e., signal strength, however, are different, meaning greater material volumes in columns compared to voids. The rod-shaped columns and surrounding voids, respectively, have been attributed to higher density materials and to lower density materials. Based on fundamental understandings, for a sputtered film, it is expected that the EDS signal from a void should be lower than that from the rod-shaped column. The difference in height between rod-shaped columns and surrounding voids is due to the different amount of elements. In addition, the large amount of elements in column versus small amount in void confirms the nonuniform surface distribution of atoms, which is associated with the limited adatom mobility in sputtered film. Note that the presence of carbon (abbreviated as C) is attributed to the ambient environment, and that oxygen (abbreviated as O) is present due to high affinity of Ti to oxygen; since the signal of O is considerably small compared to Ni and Ti, it is likely that a thin layer of TiO2 is formed.

The rod-shaped columns morphology and the amount of atoms in the columns can contribute to the grain formation. The differential grain size in BTIBD films versus sputtered films are inherently due to the different techniques BTIBD versus magnetron sputtering. Admittedly, the different thickness and heat treatment protocols can affect the grain size; however, the following observations suggest that the dominant factor influencing grain size is the nucleation barrier associated with the different smoothness (or film morphology) for BTIBD versus magnetron sputtering: compared to the sputtered film in Fig. 1, the sputtered film with the same composition but larger thickness (120 nm) in Fig. 2(c) underwent higher temperature treatment, and still gave rise to the grain size on the same order as in Fig. 2(f). Moreover, for different compositions, 42.4 at. % Ni in Figs. 2(a) and 2(d), and 52.1 at. % Ni in Figs. 2(b) and 2(e), the same order of grain size has been observed, albeit different temperature and/or time. Despite the different composition, thickness, and heat treatment in sputtered films, the results show unanimously the same order of small grain size. Note in micrometer thickness films, it has been reported that as the heat-treatment temperatures increases the grain sizes grow to larger dimensions. However, for film thicknesses below 200 nm, as temperature increases, nucleation is favored over growth so that within the same area, there will be more nuclei and thus the grain sizes are constrained. Thus, at higher temperatures, smaller grain sizes are reported, and at lower temperatures, larger grain sizes were observed. It is reasonable to assume that the source of the grain size differential is the nucleation dominating for the thin film thickness on the order of 100 nm as in our work.

We postulate that the BTIBD films are conducive to crystallizing large grains. The observations that large grains were formed in BTIBD films evidenced by the discrete spot in Fig. 1(a) and the circled grains in Figs. 1 and 3 in contrast to small grains in sputtered films underscore the

Fig. 5. (Color online) (a) STEM image of sputtered NiTi thin film before heat-treatment, and (b) energy-dispersive x-ray spectroscopy profile on selected areas of site A and site B in (a). In (a), site A is on one rod-shaped column and site B is on one void. The operation conditions on site A and site B are the same.

consequences of utilizing sputtering to fabricate nanoscale thickness films. The columnar-void morphology in sputtered films may present a larger energy barrier for crystallization from the amorphous state based on the following rationale.\textsuperscript{46} Rod-shaped columns should exhibit small radii of curvature. Relative to a smooth surface, the amount of free convex surface atoms, i.e., atoms on the convex surface that are free and unbounded to the bulk, can increase significantly. Consequently, the surface tension, which is due to the force required to support the film per unit width, should be higher.\textsuperscript{46} We draw an analogy between nucleation of grains in the amorphous, solid phase of nanoscale thickness NiTi alloy films to nucleation of thin film nuclei from physical vapor deposition. The energy barrier to the film nucleation from the vapor is a cubic function of surface tension\textsuperscript{46}

\begin{equation}
\Delta G^* = \left(\frac{16}{3}\right)\gamma f \left(\frac{RT}{V_m}\ln\left(\frac{p_c}{p}\right)\right)^2,
\end{equation}

where \(\Delta G^*\) is the energy barrier to nucleation, \(\gamma f\) is the surface tension of film free surface, \(V_m\) is the molar volume of the condensate, \(T\) is the temperature, \(R\) is the gas constant, \(p_c\) is saturation vapor pressure, and \(p\) is the pressure above \(p_c\). Likewise, the energy barrier for nucleation of grains from the amorphous film can be a cubic function of surface tension. The rod-shaped columns are prevalent in the sputtered films and absent for the BTIBD films, and thus, the sputtered films should have significantly higher surface tension and energy barrier. We believe that this disparity between magnetron sputtering and BTIBD is exacerbated for the nanoscale thickness films because the height differentials between the columns and the voids are drastic and prevail over a large fraction of material surface so that free surface will considerably increase. A large part of the thermal energy input via heat treatment temperatures and time is likely spent to overcome the high energy barrier for nucleation in sputtered films. Presumably, the remaining fraction of the energy is insufficient to grow grains to a substantial size. On the other hand, in the smooth BTIBD films, the low energy barrier for nucleation utilizes a small part of thermal energy, thereby allowing sufficient energy to facilitate the formation of large grains in the ultrathin films.

\section*{V. SUMMARY AND CONCLUSIONS}

In summary, BTIBD produces ultrathin NiTi films without the columnar-void surface topography observed for thin films fabricated using magnetron sputtering. BTIBD adds independent control of low energy ion flux toward the growing film, which increases the adatom mobility of the deposited atoms. The increased mobility results in smooth surfaces for as-deposited films and the smoothening is composition-independent. In sputtering, the mobility of deposited atoms is limited, resulting in columnar-void surface. The as-deposited films, from both BTIBD and sputtering, are amorphous. For the sputtered films, grain formation occurs by merging arrays of columns. We postulate that the columnar-void morphology imposes a relatively large energy barrier for crystallization so that small grains (~10 nm), which exhibit the B2 crystal structure, are present by comparison with BTIBD films. The BTIBD is promising for fabricating nanoscale thickness NiTi alloy thin films as crystallization heat-treatments produce large grains (>100 nm) with the B2 crystal structure, which are prerequisites for the shape memory mechanism.

\section*{ACKNOWLEDGMENTS}

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