Studies on the surface morphology and hydrophobic property of NiTi thin films under in situ and post annealing various temperatures

Jingzhen Zong, Kai Feng, Zhuguo Li, Abdul Mateen Qasim, Paul K Chu*<br><br>Abstract<br>Surface morphology and hydrophobic property of NiTi thin films are investigated under various in situ and post annealing temperatures. The XRD and AFM results reveal that in situ annealed NiTi thin films crystallize at lower temperature and have larger surface roughness than post annealed samples. Heating during sputtering provides energy for atoms to move to position of equilibrium, thus more regular crystal structure is observed in in situ annealed NiTi thin films. Another reason for the smoother surface observed in post annealed thin films is that large amount of Ni$_4$Ti$_3$ precipitation in hinders the formation of B19$'$ phase. The contact angle becomes larger with the increase of surface roughness and the maximum contact angle of 123.5° is achieved in 600 °C in situ annealed thin film with 41.7 nm surface roughness.

1. Introduction<br>NiTi shape memory alloy thin films have great advantage in biomedical and microelectromechanical systems (MEMS) due to their high output per volume, easy production, high damping capacity and biocompatibility [1]. Among many methods, magnetron sputtering is most commonly used for manufacturing NiTi thin films [2]. The state of the thin film is amorphous after deposited at ambient temperature, thus a subsequent heat treating process is needed to obtain shape memory effect (SME) [3,4]. For MEMS purpose, the temperature in post-annealing and in-situ annealing process is an important factor for the fabrication and properties of NiTi thin films [4–6]. Understanding the effect of post and in situ annealing process on the crystallization and microstructure of NiTi thin films is important [7,8]. While the influence of post-annealing temperature on the microstructure of NiTi thin films of various compositions has been widely studied [9–11], the role of in situ annealing temperature and the difference between post and in situ annealing on the microstructure of the film have rarely been discussed [5]. In addition, during the operation of the MEMS device, the moisture absorbed can have a negative effect on device reliability, eventually affects the operation of the MEMS structures [12]. Thus, the hydrophobic property is of great importance in the utilization of NiTi thin films.

In this work, we investigated the crystallographic structure, morphology and hydrophobicity of in situ and post annealed NiTi thin films. The role of annealing temperature and comparison between in situ annealing and post annealing were discussed in detail.

2. Experimental details<br>The NiTi films were deposited onto silicon (100) wafers using ATC ORION Sputtering System (AJA International, Inc.). TiNi alloy target with atomic ratio of 1:1, purity 99.9%, was placed on a DC power supply target. After the pressure of chamber was depressurized below 5.0 × 10$^{-7}$ Torr, Ar gas with flow rate of 10 SCCM (standard-state cubic centimeter per minute) was introduced into the chamber. The target power of NiTi was 150 W and no bias voltage was applied. The NiTi films were deposited at room temperature (not exceed 80 °C), 300 °C, 400 °C, 500 °C and 600 °C for an hour. The NiTi thin films deposited at room temperature was subjected to post annealing treatment using a laboratory-designed vacuum heat treatment furnace with auxiliary mechanical pump and diffusion pump. The vacuum chamber was pumped down to a pressure of $\leq 1 \times 10^{-3}$ Pa and heated up to 300 °C, 400 °C, 500 °C and 600 °C for 1 h.

The crystallographic structure of NiTi thin films were characterized by GIXRD on a RIGAKU D/MAX 2550 diffractometer with Cu Kα radiation.
\( \lambda = 0.15406 \) at room temperature. The incident angle was kept at 1° and the step size was 0.02°. The surface morphology of NiTi films was observed by atomic force microscopy (AFM). The water contact angle was tested using the Ramé-Hart contact angle equipment equipped with a motorized tilting stage at room temperature. Water droplets with a volume of 4 \( \mu \)L were used to determine the static water contact angle.

3. Results and discussion

The crystallography structure of NiTi thin films under various in situ and post annealing temperatures was characterized by XRD and the results are presented in Fig. 1. On a cold substrate, Ni and Ti atoms do not have enough energy to diffuse, and are dispersed

![Fig. 1. XRD patterns of post-annealed (a) and in situ annealed, (b) NiTi thin films.](image)

![Fig. 2. AFM images of as deposited (a), in situ annealed (b: 300 °C, c: 400 °C, d: 500 °C, e: 600 °C) and post-annealed (f: 300 °C, g: 400 °C, h: 500 °C, i: 600 °C) NiTi thin films.](image)
on surface. Wide peaks of as-deposited NiTi thin films in Fig. 1a and b indicate that the state of the film is amorphous. Annealed NiTi thin films contain Austenite (B2) and Ni4Ti3 precipitation. Peaks of B19' phase were observed in XRD results of in situ annealed thin films and were not observed in post annealed films. In Fig. 1a, intensity of Ni4Ti3 peaks relative to B2 peaks is higher than Fig. 1b, which indicates that post annealed NiTi thin films contain more Ni4Ti3 phase. Ni4Ti3 precipitation hinders the formation of B19' phase. Post-annealed NiTi thin films do not fully crystallize until the annealing temperature reaches 600 °C. As shown in Fig. 1b, the B2 (110) peak of in situ annealed NiTi thin films is narrower than post annealed thin films. Heating in sputtering progress provides energy for atoms to move to equilibrium position in situ annealed thin films and more regular crystal structure is observed. The temperature needed for crystallization of in situ annealed thin films is much lower than post annealed thin films.

Fig. 2 shows the AFM surface morphology of NiTi thin films. The roughness data of Table 1 was from AFM results and the grain size was calculated from XRD results. The surface of amorphous NiTi thin film deposited on a cold substrate is very smooth (Fig. 2a) and the roughness is 0.6 nm (Table 1). With the increase of in situ annealing and post annealing temperatures, the surface morphology composes of larger islands. The sputtered NiTi atoms will accumulate on a heated substrate, and are dispersed on a cold substrate, so films deposited on a heated substrate will have larger surface roughness than films deposited at a cold substrate [13]. At the same temperature, in situ annealed films have greater grain size and surface roughness than post annealed films (Table 1). The roughness of 600 °C in situ annealed films reached 41.7 nm, which increases one order of magnitude than others. And this phenomenon has not been reported before. But the surface roughness of post annealed thin films only increased slightly to 1.4 nm at 400 °C and dropped to 0.7 nm at 600 °C. These phenomena may be caused by two reasons. Firstly, the surface of martensite is rougher than austenite and post annealed NiTi thin films do not contain martensite due to large amount of Ni4Ti3 precipitation. Secondly, the nucleation and growth of grains are different between two methods. For in situ annealing, nucleation and growth process is strongly dependent on temperature [14,15]. According to Structure-Zone Model [16], as the Tdep/Tm ≤ 0.458 (Tm = 1310 °C [17] and Tdep ≤ 600), all of the in situ annealed thin films have columnar structure. The columnar structure is amorphous at ambient temperatures because the surface diffusion is limited. While at higher temperatures, bulk diffusion becomes significant and grain boundary migration takes place throughout the deposition process thus large grains with low surface energy can be observed. As shown in Fig. 2e, abnormal grain growth happened at 600 °C in situ annealing temperature. The content of B19' phase gradually increases with increasing annealing temperature in situ annealed thin films, which also leads to the increase of surface roughness. For post annealing method, circular shaped crystals are observed. Both nucleation and growth increase with the temperature, thus the competition between them leads to the slightly change of surface roughness with increasing post annealing temperature.

As shown in Fig. 3, almost all of the annealed thin films are hydrophobic surfaces with contact angles more than 90° except for as-deposited thin films (Fig. 3a) and 500 °C post annealed thin films (Fig. 3d), which have smallest surface roughness of 0.6 nm. The contact angle became larger with the increase of surface roughness. Contact angle of the surface reached 123.5° at 600 °C in situ annealing temperature (Fig. 3i). The surface topography effects have been mathematically expressed by the Wenzel equation [18]. The Wenzel equation is expressed as: \( \cos \theta = r \cos \theta_0 \), where the roughness factor \( r \) is the ratio of the true to the apparent surface areas, \( \theta_0 \) and \( \theta \) are contact angles between water and surfaces with or without rough microstructure. The rough nanostructure allows for large amount of air trapped in the gaps of the islands, enhancing the contact angle of the surface. The largest contact angle is observed in 600 °C in situ annealed NiTi thin films, which have the largest surface roughness of 41.6 nm.

### Table 1

<table>
<thead>
<tr>
<th>Annealing temperature</th>
<th>Roughness (nm)</th>
<th>Grain size (nm)</th>
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<tbody>
<tr>
<td></td>
<td>Post annealing</td>
<td>In situ annealing</td>
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<tr>
<td>Room temperature</td>
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<tr>
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<tr>
<td>400 °C</td>
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<tr>
<td>500 °C</td>
<td>1.4</td>
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<tr>
<td>600 °C</td>
<td>0.6</td>
<td>41.7</td>
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Fig. 3. Contact angle of NiTi thin films of different annealing methods. (a: as deposited, b: 300 °C, c: 400 °C, d: 500 °C, e: 600 °C post annealed, f: 300 °C, g: 400 °C, h: 500 °C, i: 600 °C in situ annealed.)

### 4. Conclusions

Crystallographic structure and surface roughness of magnetron sputtered NiTi thin films strongly depend on the annealing temperature and the annealing methods. In situ annealed thin films crystallize at lower temperature than post annealed thin films due
to energy provided by heating in sputtering for atoms to move to position of equilibrium. Higher surface roughness of in situ annealed thin films is caused by two reasons. Firstly, large amount of Ni₄Ti₃ precipitation in post annealed thin films hinders the formation of B19′ phase. Secondly, nucleation and growth of grains of two methods are different. With the increase of in situ annealing temperature, surface roughness and hydrophobic property are enhanced. Maximum hydrophobic effect of 123.5° contact angle is achieved in thin films deposited at 600 °C in situ annealing temperature with 41.7 nm roughness.

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