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Role of the substrate on the growth of Ni-Ti sputtered thin films

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Abstract

Ni-Ti thin films have been recognized as promising and high performance materials in the field of microelectromechanical system applications. However, important issues like formation of film texture and its control are still unresolved. Widening the scope of previous experiments concerning the influence of the deposition parameters on the Ni-Ti films structure, here we show how different crystallographic orientations can be obtained by changing the substrate type. The growth of near-equiaxial Ni-Ti films, deposited by magnetron co-sputtering from Ni-Ti and Ti targets on heated substrates ($\approx 470^\circ\text{C}$), has been studied *in situ* by x-ray diffraction at a synchrotron radiation beamline. As mentioned in other studies for depositions on Si(100), a (110) fiber texture is observed for the B2 phase. However, a preferential stacking of (100) planes of the B2 phase parallel to the film surface was observed when using a MgO(100) substrate. The preferential orientation of B2(100) // MgO(100) was very strong and was kept as such until the end of the deposition, which lasted for 7.2 ks (≈ 900 nm). Ni-Ti films were also deposited on a TiN layer (≈ 15 nm) previously deposited on top of a SiO₂/Si(100) substrate. In this case, a crossover from (110) oriented grains dominating at small thicknesses, to (211) oriented grains taking over at larger thicknesses was observed. These are promising results concerning the manipulation of the crystallographic orientations of Ni-Ti thin films, since the texture has a strong influence on the extent of the strain recovery.

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Keywords: structure and morphology, deposition by sputtering, *in-situ* x-ray diffraction

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1. Introduction

Ni-Ti Shape Memory Alloy thin films exhibit high recoverable strains and large recovery forces. They can be electrically driven using joule heating, and they demonstrate fast cooling rates when compared with the bulk material because of their higher surface/volume ratio of materials increasing substantially the heat transfer rate. Their compatibility with batch-processing technology of silicon micromachining is also a plus for the desired merging of the silicon-based microelectronics with micromachining technologies, enabling complete systems-on-a-chip to be realized [1].

Several studies have been published concerning the deposition of Ni-Ti thin films [2, 3]. They are usually prepared using a sputtering method and typically deposited on Si and on SiO₂/Si wafers. However, there are still important issues unresolved like substrate effects as well as formation of film texture and its control. It is essential to evaluate the crystallographic texture of the Ni-Ti thin films, since it has a strong influence on the extent of the strain recovery, and strong textures may thus lead to anisotropic shape memory behaviour [4]. In the present study, *in-situ* x-ray diffraction (XRD) during the growth of Ni-Ti thin films was chosen in order to investigate their texture development on naturally oxidized Si(100), MgO(100) and TiN/SiO₂/Si(100) substrates.

2. Experimental

The Ni-Ti films were deposited by DC magnetron sputtering in a chamber specially designed for *in-situ* x-ray measurements. Details of the growth chamber are given in Ref. [5]. Two unbalanced magnetrons, equipped with a 25.4 mm Ni-Ti target (49 at% Ni – 51 at% Ti) and a 25.4 mm Ti target (purity 99.99%), respectively, were positioned at a distance of 100 mm from the substrate and tilted 30° away from the substrate normal. Three different types of substrates were used: (1) a 15×15 mm² naturally oxidized Si(100) wafer, (2) a 10×10 mm² polished MgO(100) wafer and (3) a TiN layer (≈ 15 nm) previously deposited on top of a SiO₂/Si(100) substrate. The base pressure at the deposition temperature of ≈ 470°C was 2×10⁻⁵ Pa and the working pressure during deposition was 0.42 Pa. The MgO substrate was reconstructed and thermally degassed by heating to 690°C for 3.6 ks. For the deposition of the TiN buffer

layer, the Ti target was run at a constant power of 80 W with an Ar/N₂ gas flow of 2/0.5 sccm. A negative bias voltage of -30 V was applied to the substrate during the deposition of TiN. The Ni-Ti and Ti magnetrons were driven at a power of 40 and 20 W, respectively, during ≈ 7.2 ks, without bias resulting in final thicknesses of approximately 900 ± 80 nm and compositions of roughly 50 at% Ni - 50 at%Ti.

The deposition chamber, equipped with Kapton windows for XRD was mounted on the six-circle goniometer at the ROBL beamline at the European Synchrotron Radiation Facility in Grenoble. The x-rays were monochromatized to $\lambda = 0.675 \text{ \AA}$ (18.367 keV) in order to bring the relevant Bragg peaks into the window openings. During film deposition and during subsequent annealing, repeated Bragg-Brentano, i.e. coupled $\theta-2\theta$ scans were carried out, thus probing the diffraction vector perpendicular to the plane of deposition. Low angle specular reflectivity time resolved at a fixed incidence angle was also employed to determine the growth mode for the deposition on MgO(100). The time-resolved specular reflectivity signal resembles the technique of reflective high-energy electron diffraction (RHEED) and thus can be used to observe changes in the surface morphology during growth on an atomic scale [6-8], from which the growth mode of the developing film can be derived.

The pole figures have been determined for $0^\circ < \chi < 85^\circ$ and ϕ -scans in the range $0^\circ < \phi < 360^\circ$, both with increments of 5° , at a laboratory source with Cu-K α radiation (BRUKER AXS D5005).

3. Results and discussion

Fig. 1 shows a diffractogram obtained after deposition (at the austenitic state) for the Ni-Ti film deposited on naturally oxidized Si(100) substrate. The variation of the integrated intensities of the (110) and (200) peaks of the B2 phase as well as the variation of the lattice parameter a_0 can be found in Ref. [9]. Gisser *et al.* [10] reported in early studies that when the Ni-Ti films are crystallized during the deposition process they are highly oriented, with the B2(110) face parallel to the (100) face of the silicon wafer. For most bcc metals the lowest surface energy corresponds to the (110) surface, as predicted by

lattice calculations [11]. This should thus also lead to the preferential growth of (110) planes of the Ni-Ti B2 phase parallel to the substrate surface.

Fig. 2 shows the time-dependent x-ray specular reflectivity for the first 163 s of the Ni-Ti deposition on the MgO(100) substrate. The intensity was recorded at intervals of 1 s, starting 60 s before the shutter was opened and the deposition began. The arrow indicates the moment when the shutter was closed again. Intensity oscillations are depicted showing heteroepitaxial layer-by-layer growth, with increased surface roughening. The *in situ* XRD measurements have shown a preferential stacking of (100) planes of the B2 phase parallel to the film surface. The preferential orientation of B2(100) // MgO(100) was very strong and was kept as such until the end of the deposition, which lasted for 7.2 ks (\approx 900 nm). The pole figures confirm a strong (100) fiber texture (Fig. 3).

Kim *et al.* [12] proposed that a stronger interfacial adsorption on the heated substrate promotes the preferential coverage by a first layer of Ti on top of SiO₂/Si and MgO(100) substrates. This leads to the preferential formation of the (h00)-oriented Ni-Ti film since, in the B2 cubic structure, the (h00) planes are alternately occupied by Ni and Ti atoms. The crystal structure of MgO is NaCl structure with the lattice constant of 0.421 nm. If one considers that the interatomic distance of oxygen is 0.297 nm for the MgO(100) plane, and the interatomic distance of titanium is 0.301 nm for the NiTi(100) plane, the misfit between their interatomic distance is only approximately 1.3%. This is in agreement with the behaviour observed by low angle specular reflectivity time resolved for the growing mode of the first few monolayers, which shows a good adaptation of the Ni-Ti structure to the MgO(100) substrate. The pole figures also show that the stacking of the Ni-Ti B2 phase on the MgO(100) substrate occurs with a disparity of 45° suggesting that the Ti-O adsorption sites between the Ni-Ti and oxide substrate are essential to improve the (100) orientation of the B2 phase.

On the TiN layer, the diffraction peak B2(110) also appeared from the beginning of the deposition. However, the B2(211) peak was also detected with a crossover from (110) oriented grains dominating at small thicknesses to (211) oriented grains taking over at larger thicknesses as seen in Fig. 4.

Apparently, the TiN buffer layer has an important role in the appearance of the (211) orientation parallel to the substrate. Most likely, already since the beginning of the deposition, grains with (211) planes parallel to the substrate are present. An initial competitive growth between the (211) and (110) crystal orientations – competition between the orientation induced by the substrate and the one which minimizes surface energies – occurs. The (211) orientation gradually overgrows the (110) orientation. We suggest that the fact that the targets are tilted 30° away from the substrate normal has a considerable role on the later development of the (211) orientation parallel to the substrate. Work is in progress to investigate the texture through the realization of pole figures.

4. Conclusion

This study shows that the substrate plays an important role on the crystallographic orientations of Ni-Ti thin films. The Ni-Ti films were crystallized during the deposition process. A (110) fiber texture is observed for the B2 phase for depositions on Si(100). Using a MgO(100) substrate, a strong preferential stacking of (100) planes of the B2 phase parallel to the film surface could be induced. In this work, using a TiN layer (≈ 15 nm) previously deposited on top of a SiO₂/Si(100) substrate, a crossover from (110) oriented grains dominating at small thicknesses, to (211) oriented grains taking over at larger thicknesses was observed. A TiN buffer layer is thus a promising tool concerning the manipulation of the crystallographic orientations of Ni-Ti thin films.

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References

- [1] H. Kahn, M.A. Huff, A.H. Heuer, J. Micromech. Microeng. 8 (1998) 213-221.
- [2] Y. Fu, H. Du, W. Huang, S. Zhang, M. Hu, Sens. Actuators A 112 (2004) 395-408.
- [3] B. Winzek, S. Schmitz, H. Rumpf, T. Sterzl, R. Hassdorf, S. Thienhaus, J. Feydt, M. Moske, E. Quandt, Mater. Sci. Eng. A 378 (2004) 40-46.
- [4] Y.C. Shu, K. Bhattacharya, Acta mater. 46 (1998) 5457-5473.
- [5] W. Matz, N. Schell, W. Neumann, J. Böttiger, J. Chevallier, Rev. Sci. Instrum. 72 (2001) 3344-3348.
- [6] N. Grandjean, J. Massies, P. Venegues, M. Leroux, F. Demangeot, M. Renucci, J. Frandon, J. Appl. Phys. 83 (1998) 1379-1383.
- [7] E. Weschke, C. Schüssler-Langeheine, R. Meier, G. Kaindl, C. Sutter, D. Abernathy, G. Grübel, Phys. Rev. Lett. 79 (1997) 3954-3957.
- [8] J. Böttiger, J. Chevallier, J. H. Petersen, N. Schell, W. Matz, A. Mücklich, J. Appl. Phys. 91 (2002) 5429-5433.
- [9] R.M.S. Martins, N. Schell, M. Beckers, K.K. Mahesh, R.J.C. Silva, F.M.B. Fernandes, Appl. Phys. A, Mater. Sci. & Proc. 84 (2006) 285-289.
- [10] K.R.C. Gisser, J.D. Busch, A.D. Johnson, A.B. Ellis, Appl. Phys. Lett. 61 (1992) 1632-1634.
- [11] J.-M. Zhang, F. Ma, K.-W. Xu, Surf. Interface Anal. 35 (2003) 662-666.
- [12] I.-J. Kim, H. Nanjo, T. Iijima, T. Abe, Jpn. J. Appl. Phys. 29 (2000) 568- 571.

FIGURE CAPTIONS

Fig. 1. XRD diffractogram from the Ni-Ti sample deposited on naturally oxidized Si(100) (at the austenitic state).

Fig. 2. Time-dependent *in situ* specular x-ray reflectivity for the first minutes of deposition of the Ni-Ti film on MgO(100) substrate.

Fig. 3. Pole figures of Ni-Ti B2 phase grown on MgO(100) substrate, nominally measured in the Bragg peaks B2(110), B2(200) and B2(211).

Fig. 4. The integrated intensities of the Bragg-Brentano B2(110), B2(200) and B2(211) diffraction peaks, recorded as a function of time after start of film growth. The Ni-Ti film was deposited on a TiN layer (≈ 15 nm) previously deposited on top of a SiO₂/Si(100) substrate.

Fig. 1.

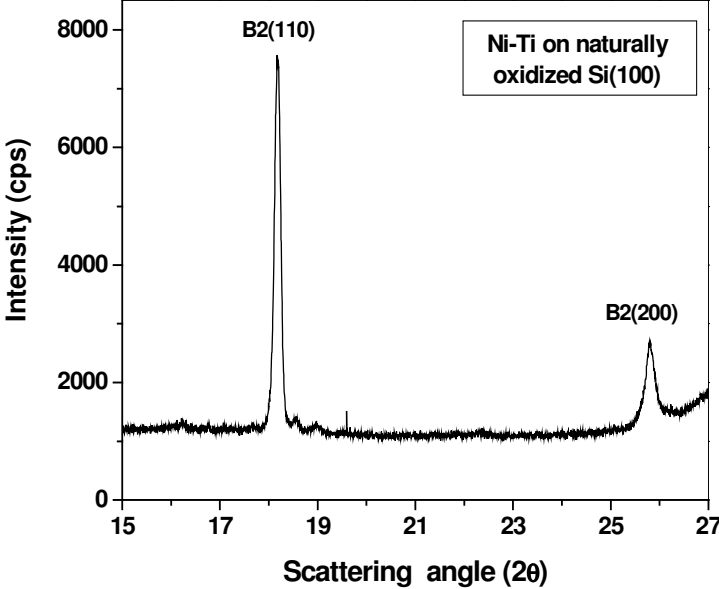


Fig. 2.

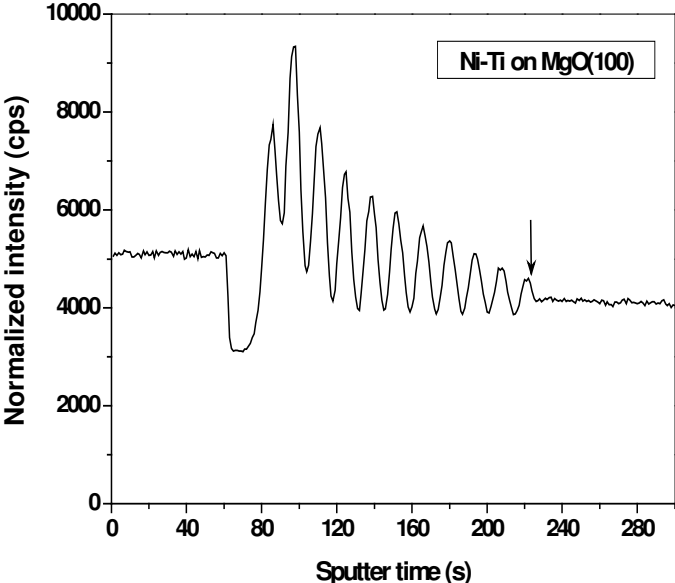
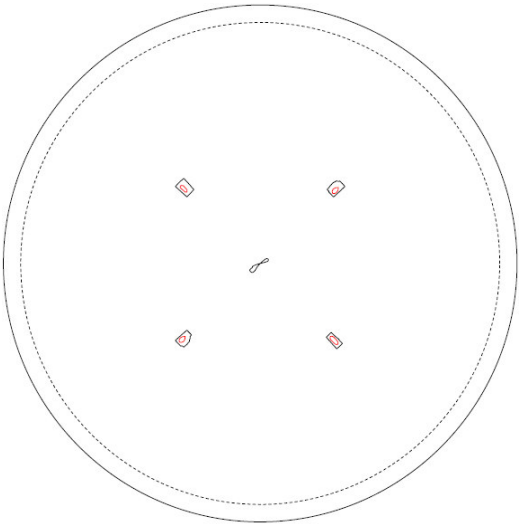
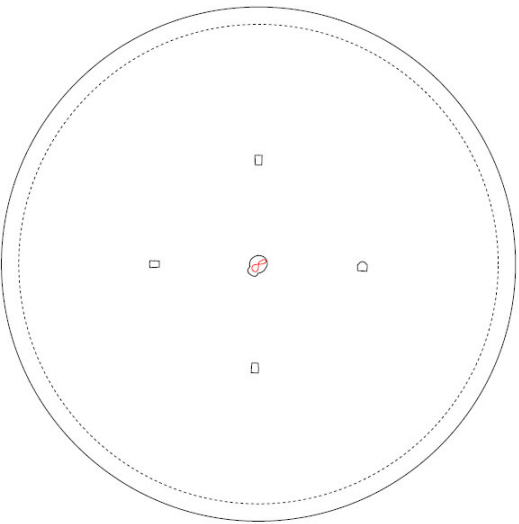


Fig. 3.

110



200



211

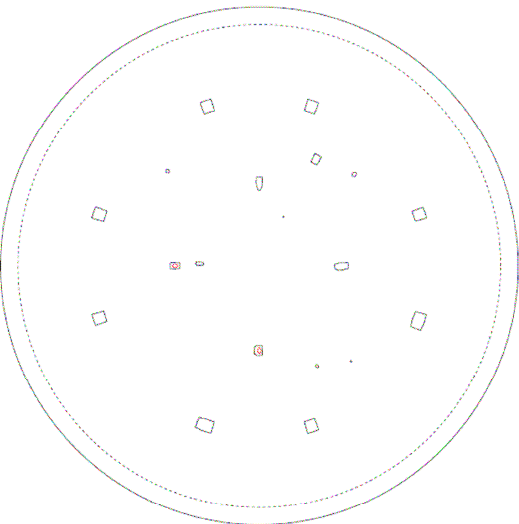


Fig. 4.

