In-situ XRD during sputtering of Shape Memory Alloy (SMA) Ni-Ti thin films

R.M.S. Martins[1,2,3], F.M. Braz Fernandes[3], R. Silva[3], M. Beckers[2], N. Schell[1,2]

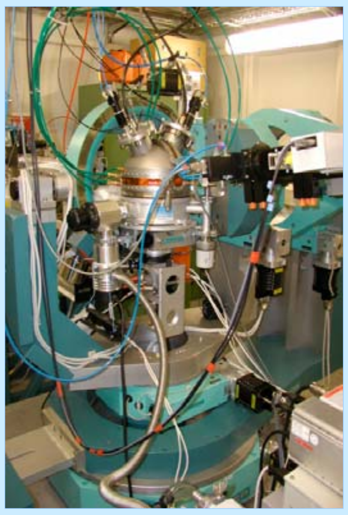
[1] ROBL-CRG at ESRF, BP 220, 38043 Grenoble, FRANCE
[2] Institute of Ion Beam Physics and Materials Research, Forschungszentrum Rossendorf, P.O. Box 510119, 01314 Dresden, GERMANY
[3] CENIMAT, FCT-UNL, Campus da Caparica, 2829-516 Caparica, PORTUGAL

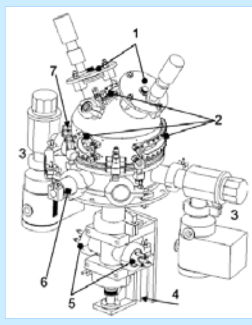
Abstract: Ni-Ti thin films present great advantages for the fabrication of micro-actuators [1]. Its structural evolution has been followed *in situ* by XRD during sputter deposition and during annealing. The series of first experiments on *in-situ* sputtering (Ni-Ti) and co-sputtering (Ni-Ti + Ti) led to a much better understanding of the structural development of the Ni-Ti films and its correlation with the corresponding deposition parameters.
The sequence of the phases formation and their preferential orientations had been followed for different deposition conditions and substrate type.

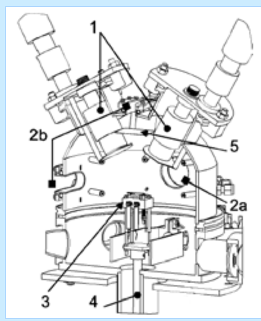
Experimental Setup

A sputter deposition chamber for the *in-situ* study of film growth by synchrotron x-ray diffraction and reflectivity was used [2]. The two magnetrons are placed at a distance of 100 mm from the substrates and tilted 30 degrees away from the substrate normal. To avoid cross contamination of the targets, chimneys (1 inch long) are mounted on the magnetrons. Air–pressure-controlled shutters are placed in front of the chimneys. Substrate heating up to 650 °C and different substrate bias voltage are possible. All the depositions were carried out with substrate heating at 470ºC. Annealing after deposition was also at 470ºC, except for sample 13 where 545ºC annealing was also used.

The deposition chamber was mounted on the six-circle goniometer in MRH.
The incident x-rays were monochromatized to *18.367 keV* (λ = 0.675 Å).
To study the growth of NiTi films in-situ, two different scattering geometries were used: Vertical Bragg-Brentano large scattering (XRD), Low-angle specular reflectivity with information on film thickness.







1. Magnetron, 2. X-ray windows, 3. Throttle valves and turbomolecular pumps, 4. Precision z-drive for substrate height alignment, 5. Electrical feedthroughs, 6. Liquid nitrogen trap, 7. Additional gas inlets.

- Magnetron with shuttters, 2a. Entrance window for the incoming beam, 2b. Exit window for the diffracted beams, 3. Substrates carrier with heater and bias voltage, 4. Tube to the z drive , 5. Window protection foils.

Diffractometer of beamline BM20 at the ESRF (ROBL-CRG) and perspective views of the sputter deposition chamber.

Thin films production

Experimental parameters:

- Base pressure lesser than 3×10^{-6} mbar,
- Target material Ni-Ti (49 at% Ni - 51 at%Ti) and pure Ti (99.99%),
- Sputter gas Ar (99.9996%) at a pressure of 3.5×10^{-3} mbar,
- The substrate temperature varied from *460 to 480ºC* during deposition.

The properties of Ni-Ti thin films are strongly dependent on the chemical composition. The chemical composition of Ni-Ti sputtered films may deviate by up to 2 at% (lower Ti) when compared to the target composition [3]; this deviation gives rise to lower transformation temperature ranges. In order to ensure transformation temperatures above room temperature, sputtering using multiple targets is an obvious solution.

At ROBL (BM20), experimental *in situ* studies of the structural evolution during sputtering (using a single target Ni-Ti) and co-sputtering (using Ni-Ti and Ti targets) were carried out.

Parameters used for sputtering deposition

Ni-Ti

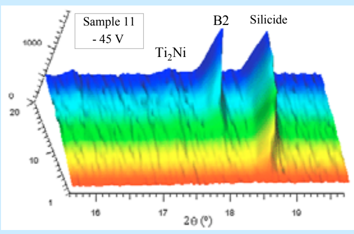
Sample	Power (W)	Substrate	Bias (V)	Deposition (min)	Annealing (min)
2	40	SiO2/Si (100)	-45	154	90
3	40	Si (100)	0	139	70
4	40	Si (100)	-45	120	62
5	40	SiO2/Si (100)	0	124	98

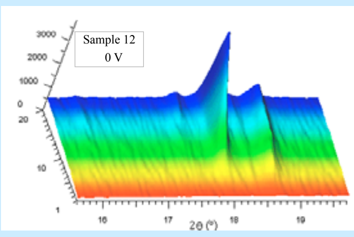
Ni-Ti + Ti

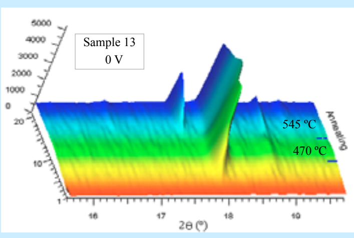
Sample	Power (W)		Substrate	Bias (V)	Deposition procedure	Annealing (min)
	Ni-Ti	Ti				
11	40	5	Si (100)	-45	4 × (35 min Ni-Ti + Ti co-sputtering / 25 min annealing)	85
12	40	5	Si (100)	0		90
13	80	5	Si (100)	0	1h 30 min (Ni-Ti + Ti co-sputtering)	46 at 470ºC 100 at 545ºC

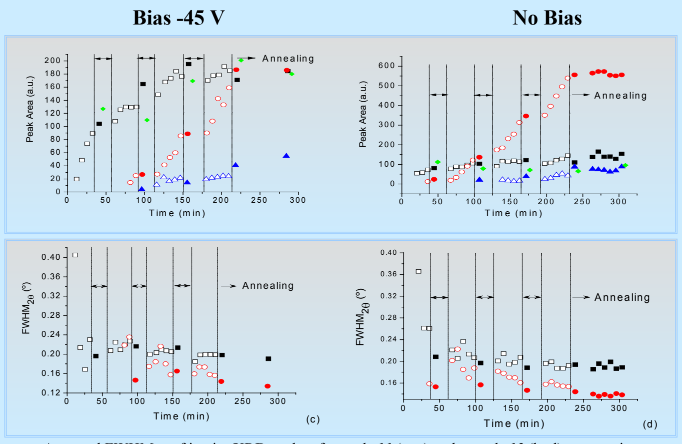
Experimental results

Co-sputtering using Ni-Ti + Ti targets



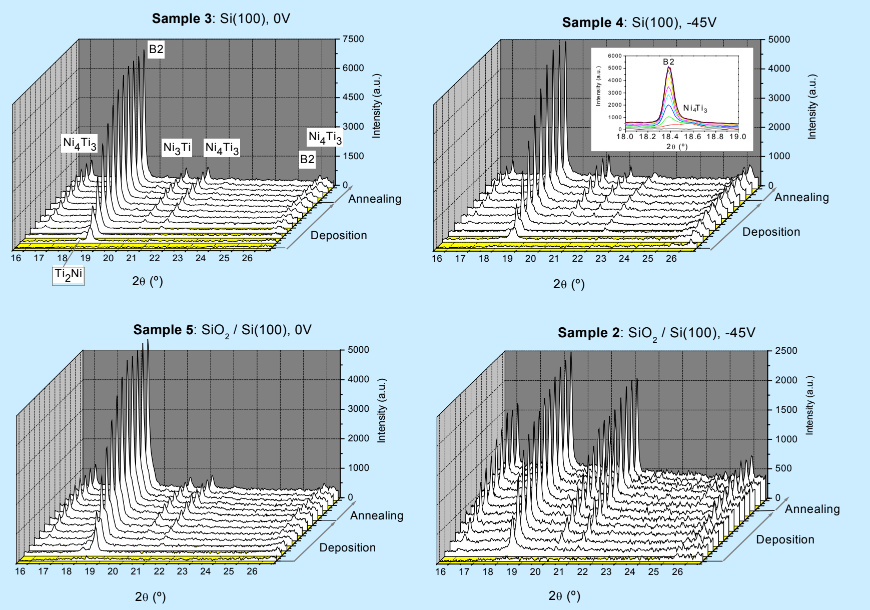






Area and $FWHM_{2\theta}$, of in-situ XRD peaks of *sample 11* (a, c) and *sample 12* (b, d), *versus* time.
(□)/(■) Ti_2Ni (Deposition/Annealing); (○)/(●) {110}B2; (●) {200}B2; (△)/(▲) Silicide.

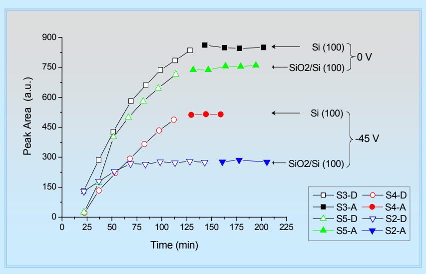
Sputtering using Ni-Ti target



Summary

This study presents the first reported experiments on in situ analysis of the sputtering of Ni-Ti thin films. These results show that:

- during co-sputtering (Ni-Ti + Ti targets), there is a significant formation of a silicide preceding the growth of the B2 phase;
- also during co-sputtering, the first layers of B2 stack preferentially on {h00} planes;
- on the other hand, during sputtering using a single target (Ni-Ti), the preferential stacking on {110} is present since the beginning of the deposition and there is not such a notorious formation of silicide as it is observed in co-deposition;
- during sputtering using a single target Ni-Ti, there is a significant formation of Ni-rich precipitates; when a bias is applied, there is a much more significant change of the peak intensities of the precipitates Ni_3Ti and Ni_4Ti_3 for the deposition on SiO_2/Si(100), compared to the one on Si(100);
- in both cases, there is a significant decrease in intensity of the B2{110} intensity when a bias (- 45 V) is applied;
- also in both cases, during the annealing (at 470ºC) after deposition, the intensity of the B2 {110} peak does not increase; for sample 2 this stabilization is reached during the deposition period;
- the FWHM changes significantly during deposition and remains quite stable during intermediate annealing; this trend is more noticeable when no bias is applied.



Evolution along time of the area of B2{110} in-situ Bragg-Brentano diffraction peaks, recorded during:
(*D*) : deposition
(*A*) : annealing that follows deposition.

Acknowledgements

The authors would like to acknowledge the financial support from ESRF for the experiment ME-584 and from the FCT/MCT for the pluriannual financial support of CENIMAT.

ROBL-CRG at ESRF, BP 220, 38043 Grenoble, France
E-mail: rui.martins@esrf.fr (R.M.S. Martins);
Tel: +33 (0)476882872; Fax: +33 (0)476882505

References

[1] A. Ishida and V. Martynov, MRS Bulletin, February 2002, p. 111.
[2] W. Matz, N. Schell, W. Neumann, J. Bottiger, and J. Chevallier, Rev. Sci. Instrum. 72 (2001), p. 3344.
[3] K. Ho, K. Mohanchandra and G. Carman, Thin Solid Films, 413 (2002), p. 1.

Materials Science Department / CENIMAT-FCT/UNL, 2829-516 Caparica, Portugal
E-mail: fbf@fct.unl.pt (F.M. Braz Fernandes);
Tel: +351 21 2948562; Fax: +351 21 2948558