Structural *in-situ* investigation of Shape Memory Alloy (SMA) Ni-Ti thin films

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Abstract: Ni-Ti SMA thin films formed by sputtering have been attracting great interest as powerful actuators in micro-electromechanical systems (MEMS) such as micro-valves, micro-fluidic pumps and micro-manipulators. Successful implementation of Ni-Ti micro-actuactors requires a good understanding of the relationship among processing, micro-structure and properties of Ni-Ti thin films. At the ROssendorf BeamLine (ROBL-CRG) at ESRF, we carried out a series of experiments that clearly illustrate the benefit of *in-situ* studies, not only during annealing, but also *during sputtering*. The *in-situ* annealing experiments, using a Be-dome furnace installed into the six-circle diffractometer of the Materials Research Hutch (MRH) allowed us to determine the **kinetics of the phenomena**, to identify the **sequence of precipitation** and to **correlate the build-up of the final structure with the processing conditions**. The *in-situ* sputtering experiments during film growth were performed using a magnetron sputter deposition chamber also installed into the six-circle diffractometer. This facility allowed us to **follow, almost in "real time", the structural evolution of the deposited thin film** as a consequence of changing deposition parameters.

In-situ GIXRD during crystallization of Ni-Ti sputtered thin films

Thin Ni-Ti films as-sputtered are amorphous if the substrate is not heated and, thus, have to be heat-treated to induce crystallization in order to show shape memory. The films have been prepared by dc magnetron sputtering. The crystallization of these films has been studied by *in-situ* GIXRD, allowing to establish a correlation between the deposition conditions and the tendency for crystallization.

Annealing has been carried out in a vacuum furnace, covered by a hemispherical Be dome (vacuum better than 2×10^{-6} mbar). The crystallization temperature has been monitored by a thermocouple fixed to the sample surface. The crystallization kinetics has been studied at 430ºC. This temperature was chosen based on preliminary experiments where it was found that the crystallization should start close to 450ºC. The thermal cycles comprised heating at an average rate of 4ºC/min.

Thin film production

DC sputtering

- p_{Ar} = 1 mTorr
- ρ_{ion} = 5.75 W/cm²
- D3 : 1.4 µm
- D4 : 1.6 µm

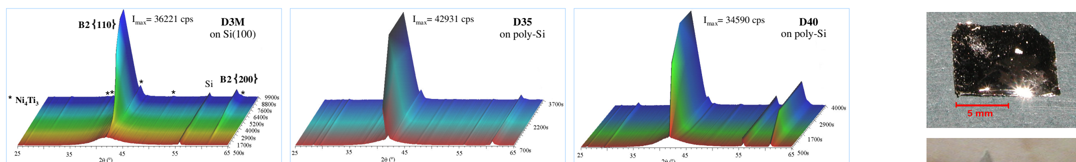
Target Composition: 49 at% Ni – 51 at% Ti

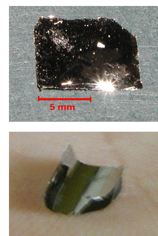
- Distance target/substrate: D3 = 70 mm, D4 = 40 mm
- D3 or D4:
  - "M" for Si(100)
  - "0" for poly-Si deposited on Si(100) at 600ºC
  - "5" for poly-Si deposited on Si(100) at 675ºC

GIXRD

Diffractometer of *ROBL* at *ESRF* and close-up view of the furnace (*arrow showing direction of incident beam).*

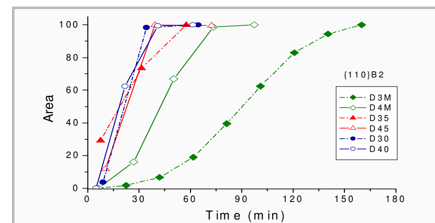
Diffraction patterns of Ni-Ti thin films during crystallization at 430ºC.





Free-standing Ni-Ti film exhibiting the two-way shape memory effect : flat on a table and bent after phase transformation on a human hand.

10×10 mm² samples were cut for investigation. Their GIXRD patterns were taken with ***1.54 Å*** radiation under grazing incidence of ***1º***.



Crystallization evolution : austenite {110} peak *versus* time during annealing at 430ºC.

The crystallization is significantly enhanced by:

- **the presence of an intermediate film of poly-silicon,**
- **the fact that the sample lies within the vertical projection of the target on the substrate.**

During crystallization Ni_4Ti_3 precipitates ⇒ two-way shape memory effect.

Using a target/substrate distance of 40 mm instead of 70 mm gives a significant change in the kinetics for deposition on Si(100) with no intermediate poly-silicon.

Summary — annealing experiments

In-situ XRD during sputtering of Ni-Ti thin films

The structural evolution has been followed *in situ* by XRD *during sputter deposition and during annealing*. The series of first experiments on 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. Also the *sequence of the phases formation* and their *preferential orientations* have been followed for different deposition conditions.

The incident x-rays were monochromatized to *18.367 keV* (λ = 0.675 Å).

To study the growth of Ni-Ti films *in situ*, two different scattering geometries were used: vertical Bragg-Brentano large angle scattering (XRD), and low-angle specular XRR with information on film thickness.

Thin film production

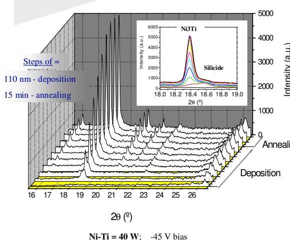
- Base pressure < 3×10^{-6} mbar
- Targets : Ni-Ti (49 at% Ni – 51 at% Ti) + Ti
- Sputter gas Ar (N6) at 3.5×10^{-3} mbar
- Distance target/substrate: 100 mm
- T = 460-480ºC during deposition / annealing after deposition at 470ºC
- Substrate: Si(100)

Diffractometer of *ROBL* at *ESRF* and perspective view of the sputter deposition chamber.

1. magnetron with shutters
2a. entrance window for the incoming beam
2b. exit windows for the diffracted beams
3. substrate holder with heater and bias voltage
4. tube to z drive
5. window protection foils

Sputtering : Ni-Ti

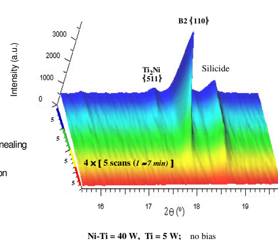
(120 min deposition / 90 min annealing)



Ni-Ti = 40 W; -45 V bias

Co-sputtering: Ni-Ti + Ti

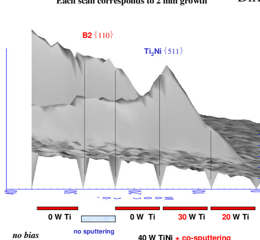
4 × (35 min Ni-Ti + Ti co-sputtering / 25 min annealing)



Ni-Ti = 40 W, Ti = 5 W; no bias

In-situ structural design

Each scan corresponds to 2 min growth



Summary — sputtering experiments

This study presents the first reported experiments of the *in-situ* analysis *during* sputtering of Ni-Ti thin films using synchrotron radiation:

- **during sputtering using a single target Ni-Ti, there is a significant formation of Ni-rich precipitates due to the loss of Ti associated with the deposition process,**
- **the first layers of B2 stack preferentially on {h00} planes,**
- **there is a significant decrease in intensity of the B2{110} peak when a bias (-45 V) is applied,**
- **during annealing the intensity of the B2 {110} peak does not increase,**
- **the FWHM changes significantly during deposition and remains quite stable during intermediate annealing; this trend is more noticeable when no bias is applied.**

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