ESRF	**Experiment title:** ***Ion bombardment of Ni-Ti thin films***	**Experiment number:** **MA-232**
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REPORT:

A negative substrate bias voltage causes a higher energetic ion bombardment of the growing film, resulting in an enhanced surface-atom mobility, but, at sufficiently high voltage, leads to defect formation. The configuration of the unbalanced magnetrons permits the plasma to extend to the region of the substrate (increasing the efficiency of the ionisation) and, thus, a greater number of ions are directed toward the growing film. When positive bias voltage is applied to the substrate, the energy of bombarding ions decreases. Conversely, when negative bias is applied, ion bombardment energy increases. Therefore, we concluded that the control of the ion bombardment energy would be one of the key factors in determining the microstructure and properties of the Ni-Ti Shape Memory Alloy (SMA) films. During this beamtime complementary tests have also been performed to complete a series of methodical investigations on Si(111), and NiTiHf on HfN/SiO_2/Si(100).

EXPERIMENTAL

The sputtering experiments were carried out in a D.C. magnetron sputtering chamber that has been described elsewhere [1]. Two unbalanced magnetrons, equipped with a 25.4 mm Ni-Ti target (51 at% Ni – 49 at% Ti) and a 25.4 mm Ti (or Hf) target (purity 99.99%), respectively, were positioned at a distance of 100 mm from the 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. For the deposition of the TiN (HfN) buffer layers, the Ti (Hf) target was run at a constant power of 80 W with an Ar/N_2 gas flow of 2/0.5 sccm and for the Ni-Ti (NiTiHf) films the Ni-Ti and Ti (Hf) magnetrons were driven at a power of 40 and 24 W (60 and 8 W), respectively. The processing conditions of the samples studied are presented in Tab. 1. Scans were run in Bragg-Brentano geometry, using 0.675 Å radiation, to reveal the type of preferential orientation during the deposition and annealing processes and to determine off-plane lattice parameters.

Sample	Substrate	Buffer layer	Substrate bias (V)		Deposition (min.)		Annealing (min.)	
			TiN (HfN) deposition	Ni-Ti deposition	Buffer layer	Ni-Ti (NiTiHf)	Buffer layer	Ni-Ti (NiTiHf)
S56	SiO_2^*/Si(100)	–	–	0	–	120 (at ≈520°C)	–	52 (at ≈520°C)
S57	SiO_2^*/Si(100)	TiN	-30	+20	41	131	31	60
S58	SiO_2^*/Si(100)	–	–	0	–	119 (at ≈520°C)	–	78 (at ≈520°C)
S59	SiO_2^*/Si(100)	TiN	-30	+20	41	124	33	55
S60	Si(111)	–	–	0	–	122	–	61
S61	SiO_2^*/Si(100)	HfN	-30	0	41	122	40	61

** 1400 Å amorphous SiO_2 capping layer*

Tab. 1: Deposition parameters for the various samples investigated.

RESULTS AND DISCUSSION

The effect of a substrate bias voltage on the growth of near equiatomic Ni-Ti thin films on a TiN buffer layer of approximately 215 nm (topmost layer formed mainly by <111> oriented grains) has been investigated in previous beamtimes [ME-1255]. The anomalous behaviour of the electrical resistivity (ER) response in Ni-Ti films is attributed to lattice distortion and twinning, which are dominant mechanisms in self-accommodation R-phase transformation. The study of the temperature dependence of the ER has shown that the degree of ion bombardment alters the phase transformation behaviour of the films. The Ni-Ti film deposited without applying a substrate bias voltage exhibits higher phase transformation temperatures. We attributed this phenomenon to the presence of higher residual compressive stress in the film. The increase of the resistivity during R-phase formation for the Ni-Ti sample deposited with a substrate bias voltage of -90 V is not as high as for the other samples probably due to structural defects created by the higher energy of the bombarding ions during film growth. SEM observations have revealed that an increase of the substrate bias voltage from -45 V to -90 V led to the appearance of surface steps on the crystals. Previously, a continuous decrease of a_o during the deposition of the Ni-Ti film without applying bias voltage (suggesting a reduction of compressive stresses with increasing thickness) has been observed [2]. Here, we have studied the effect of a positive substrate bias voltage (+20V) showing an overall decrease and practically constant value of a_o during the deposition (Fig. 1).

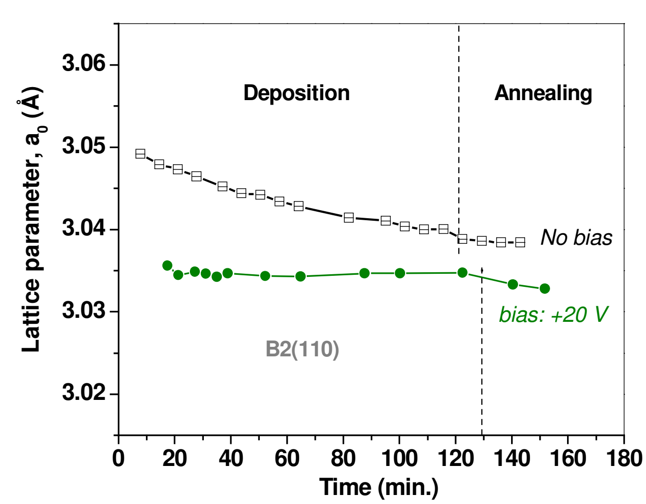

Fig. 1: Lattice parameter a_o, recorded as a function of time after start of Ni-Ti film growth on a TiN layer (≈ 215 nm). Results obtained for a Ni-Ti film deposited without applying substrate bias voltage and results obtained for a film deposited with +20 V are represented.

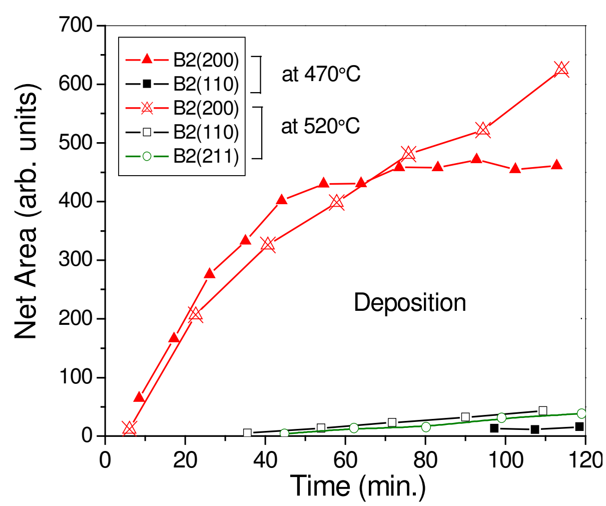

Fig. 2: Integrated intensity of the Bragg-Brentano B2 diffraction peaks recorded as a function of time for Ni-Ti films deposited on naturally oxidized Si(100), without applying substrate bias voltage, deposited at 470 and at 520°C.

As shown in Ref. [3] (results obtained during beamtime ME-936), for a Ni-Ti film deposited on thermally oxidized Si(100) at ≈ 470°C without applying a substrate bias voltage, after ≈ 540 nm film thickness, there is a stabilization of the intensity of the B2(200) peak due to a gradual change of the crystallographic direction of the growing columnar crystals. This orientation favoured the diffraction of the (310) peak of the B2 phase. In order to explore this phenomenon, a near equiatomic Ni-Ti film was deposited on thermally oxidized Si(100) without applying a substrate bias voltage but this time at a deposition temperature of ≈ 520°C. Figure 2 shows the variation of the integrated intensity of the Bragg-Brentano B2 diffraction peaks as a function of time (for both deposition temperatures). With an increase of the deposition temperature, the intensity of the B2(200) increases along the deposition process. The variation of the value of a_o as obtained from the positions of the Bragg-Brentano B2(200) peak does not exhibit such a continuous decrease during the deposition (Fig. 3). There is a convergence to a common value of a_o [values calculated using the diffraction peaks B2(200), B2(211) and B2(110)].

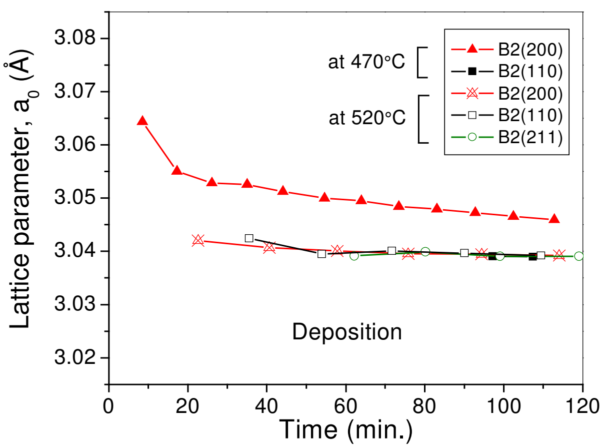

Fig. 3: Lattice parameter as obtained from the positions of Bragg-Brentano B2 diffraction peaks as a function of time for the films of *Fig. 2*.

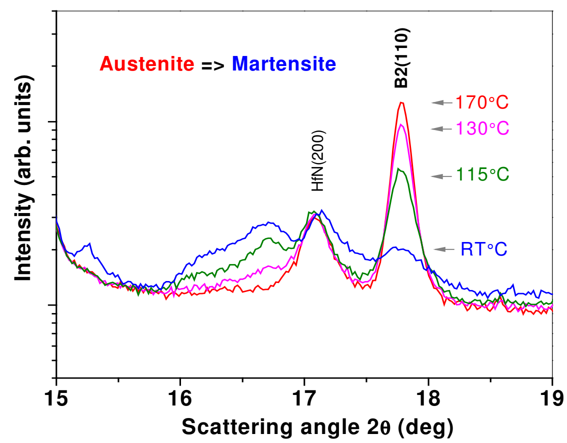

Fig. 4: XRD evaluation of phase transformation during cooling for the NiTiHf sample.

For the NiTiHf film, a preferential growth of <110> oriented grains of the B2 phase from the beginning of the deposition could be obtained using a HfN buffer layer. The higher transformation temperatures of the NiTiHf SMA, when compared to what was previously observed for Ni-Ti films, have been confirmed by XRD (Fig. 4). The deposition of Ni-Ti on Si(111) has given a preferential diffusion of Ni along <111> with $NiSi_2$ formation which was confirmed by an interface analysis by X-TEM that is presented in Ref. [4].

CONCLUSIONS

- When no substrate bias is applied, the ions bombarding the film surface during growth of the Ni-Ti film on a TiN buffer layer lead to residual compressive stress raising the transformation temperatures of the film (detected *ex-situ* by the temperature dependence of the electrical resistivity). The control of the energy of the bombarding ions is thus a tool for the manipulation of the transformation temperatures.
- The gradual change of the preferential crystallographic direction along which the columnar crystals grow (Ni-Ti films) during the deposition on SiO_2/Si(100), after an initial stacking of the B2 phase onto (h00) planes, is attributed to the combined effects of low surface mobility and shadowing (due to tilting of the magnetrons). At lower temperatures the crystallographic direction (100) shifts towards the direction of incident flux.
- The magnetron-sputtering chamber installed at ROBL proves to be a very efficient instrument to deposit, and follow *in situ* the evolution of the structure of NiTiHf films.

References

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