ESRF	**Experiment title:** ***In situ* study of the co-sputtering of ternary (Ni-Ti-X, X=Cu, Hf) SMA thin films**	**Experiment number**: **ME-1255**
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1. OBJECTIVE

Taking into account previous results obtained concerning the effect of a TiN interlayer on the subsequent growth of NiTi thin films, we decided to focus this experiment on the ternary system Ni-Ti-Hf and to complement its study with some more experiments with TiN.

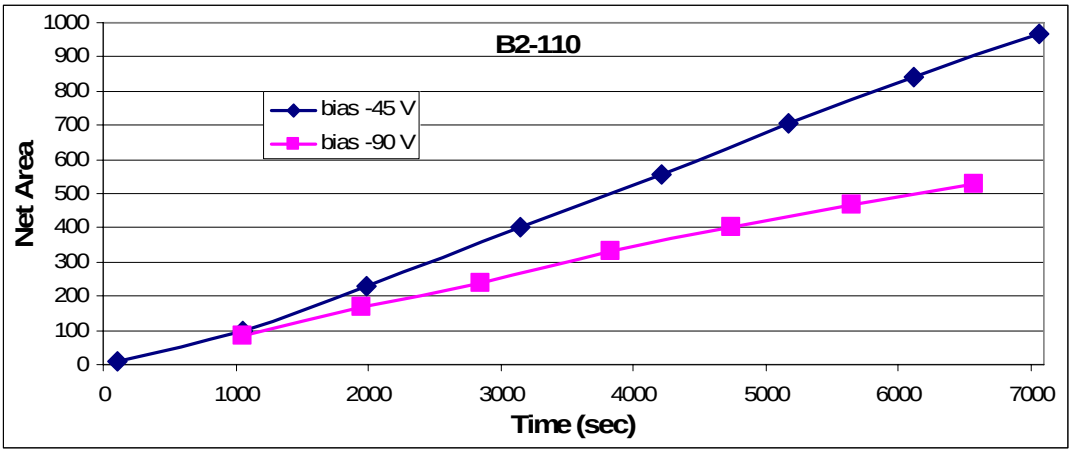
2. EXPERIMENTAL

Table 1: Deposition parameters for the various samples investigated.

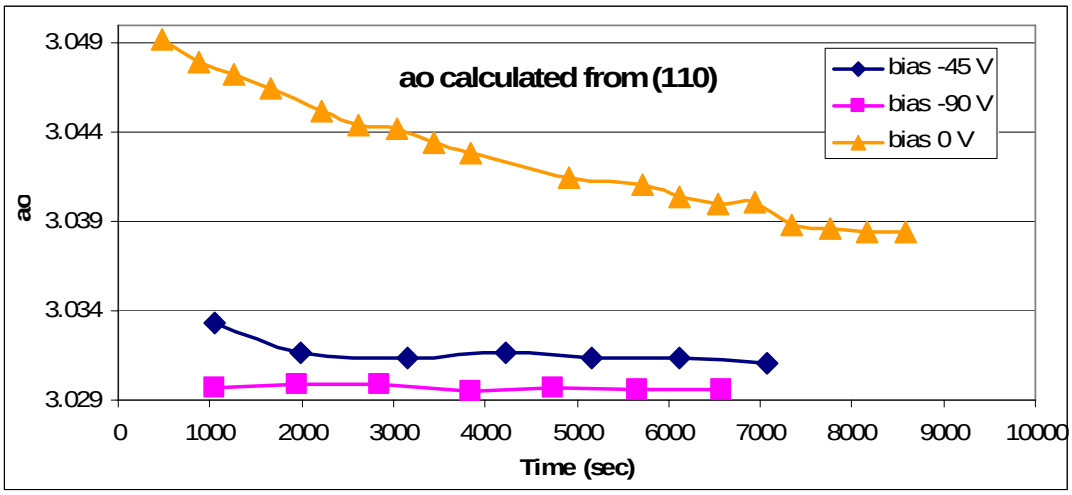
Sample	**Intermediate layer**				**Deposition**			**Remarks**
	Layer / Substrate	**Target (Power)**	**Bias (V)**	**Gas flow (Ar / N_2)**	**Targets (Power)**	**Bias (V)**	**Ar Gas flow**	
S-42	TiN / Si(100)	Ti (80 W)	-30	10.0 / 2.5 (sccm)	NiTi (40W) / Ti (20 W)	-45	4.7 (sccm)	effect of **TiN(111)** on the deposition of NiTi ***with* bias**; to be compared with **S31** (NiTi deposition ***without* bias)**
S-43					NiTi (40W) / Ti (20 W)	-90		effect of **TiN(111)** on the deposition of NiTi ***with* bias (90 V)**; to be compared with **S31** (NiTi deposition ***without* bias)** and S42 (bias = -45 V).
S-44					NiTi (40W) / Ti (20 W) + NiTi (40W) / Ti (25 W)	-45		effect of **TiN(111)** on the deposition of NiTi **with variable power (Ti target)**: **1 h (Ti, 20 W)+ 1 h (Ti, 25 W)**
S-45	HfN / Si(100)	Hf (80 W)	-30	10.0 / 2.5 (sccm)	NiTi (60W) / Hf (18 W)	-45	4.7 (sccm)	effect of **HfN(111)** on the deposition of NiTiHf: **NiTi (60 W) / Hf (18 W)**.
S-46					NiTi (60W) / Hf (8 W)			effect of **HfN(111)** on the deposition of NiTiHf: **NiTi (60 W) / Hf (8 W)**.
S-47					NiTi (60W) / Hf (13 W)			effect of **HfN(111)** on the deposition of NiTiHf: **NiTi (60 W) / Hf (13 W)**.

3. RESULTS AND DISCUSSION

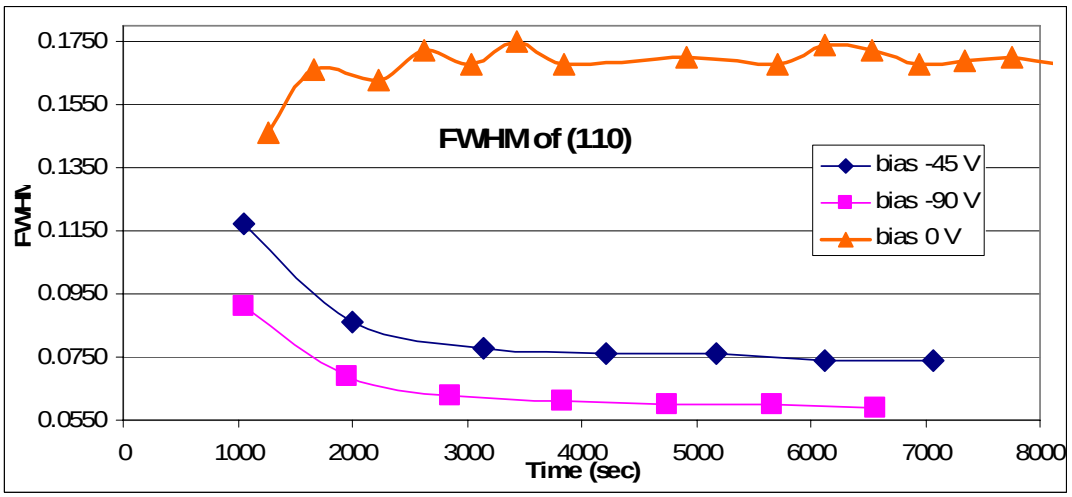
3.1 NiTi / TiN



(a)



(b)



(c)

Fig. 1: Effect of the bias applied during NiTi deposition on (a) the B2(110) net area, (b) a_o (calculated from 110) and (c) $FWHM_{(110)}$.

The NiTi / TiN experiments aimed to study the effect of the TiN intermediate layer on the growth of the NiTi film, for:

- 2 different bias voltage (-45 and -90 V) applied during NiTi deposition,
- 2 different power levels applied to the Ti target (20 W and 25 W).

The bias increase from 45 to 90 V led to a significant decrease of the intensity of the B2(110) peak.

This behavior is associated with the evolution noticed for a_0, FWHM of B2(110), where:

- for the NiTi thin films, increasing the bias decreases the B2(110) intensity slightly,
- a_0 is continuously decreasing during the deposition without bias (sample S31 from ME-1087, April 2005); the deposition with -45 V applied led to a slight decrease of a_0 at the beginning, followed by a stabilisation; increasing the bias further to -90 V, leads to a practically constant value during all the deposition; it is clear that the a_0 value is decreasing for increasing bias, approaching the equilibrium value of 3.03 Å; this trend may be interpreted as being associated with a relaxation of biaxial compressive stress states on the plane of the film;
- the decrease in the FWHM value as a funciton of the increase in the applied bias during deposition may be related to an overall trend of increasing coherence domain length with increasing bias applied during deposition,
- changing the Ti target power from 20 to 25 W made the NiTi thin film to be constituted by a lower half layer equiatomic and an upper half layer Ti-rich (presence of Ti_2Ni precipitates).

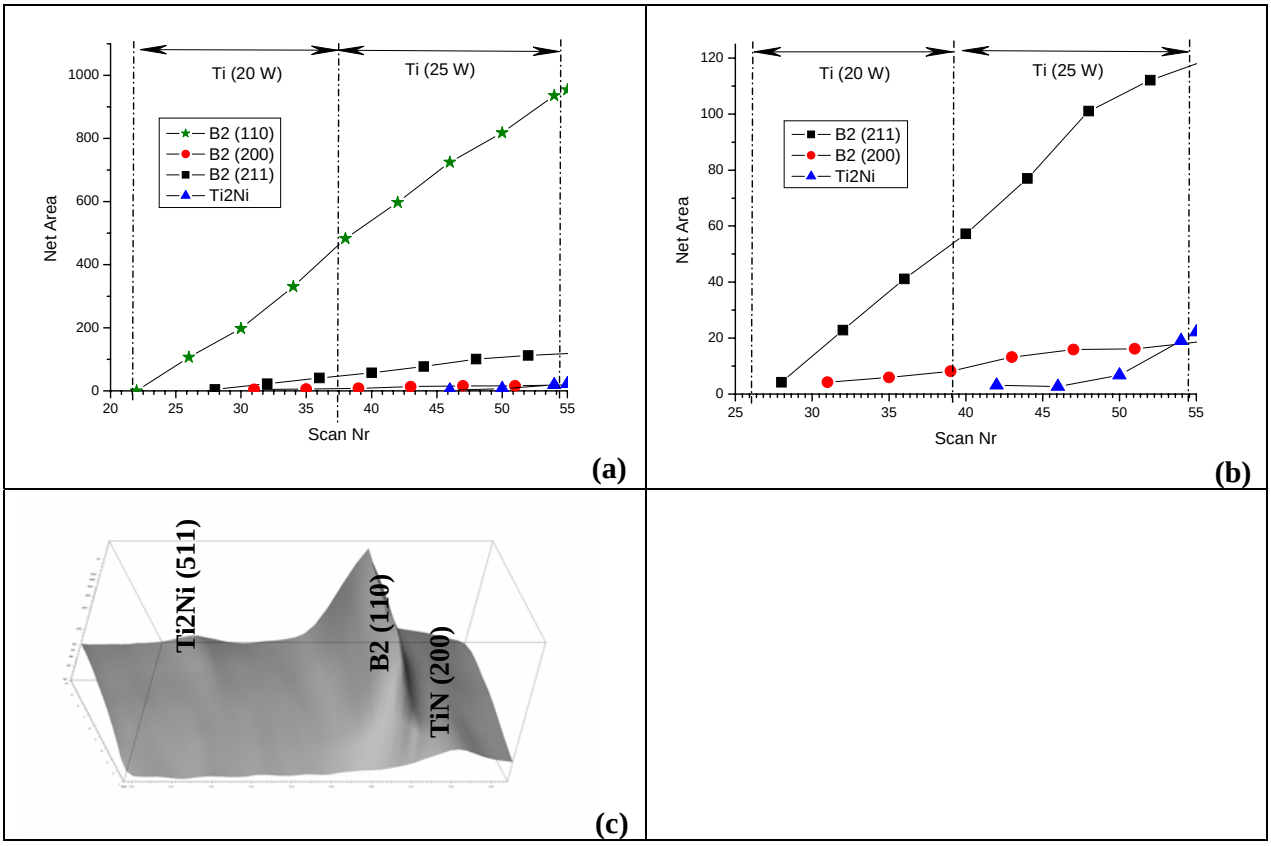


Fig. 2: XRD results from sample **S-44** (varying power of the Ti target).

(a) Variation of the net area of the diffraction peaks (110), (200) and (211) from B2 and (511) from Ti_2Ni.
(b) Zoom of the net area axis of (a).
(c) 3D representation of diffrcation peaks in the 2Θ scattering angle range from 16.9 to 19º.

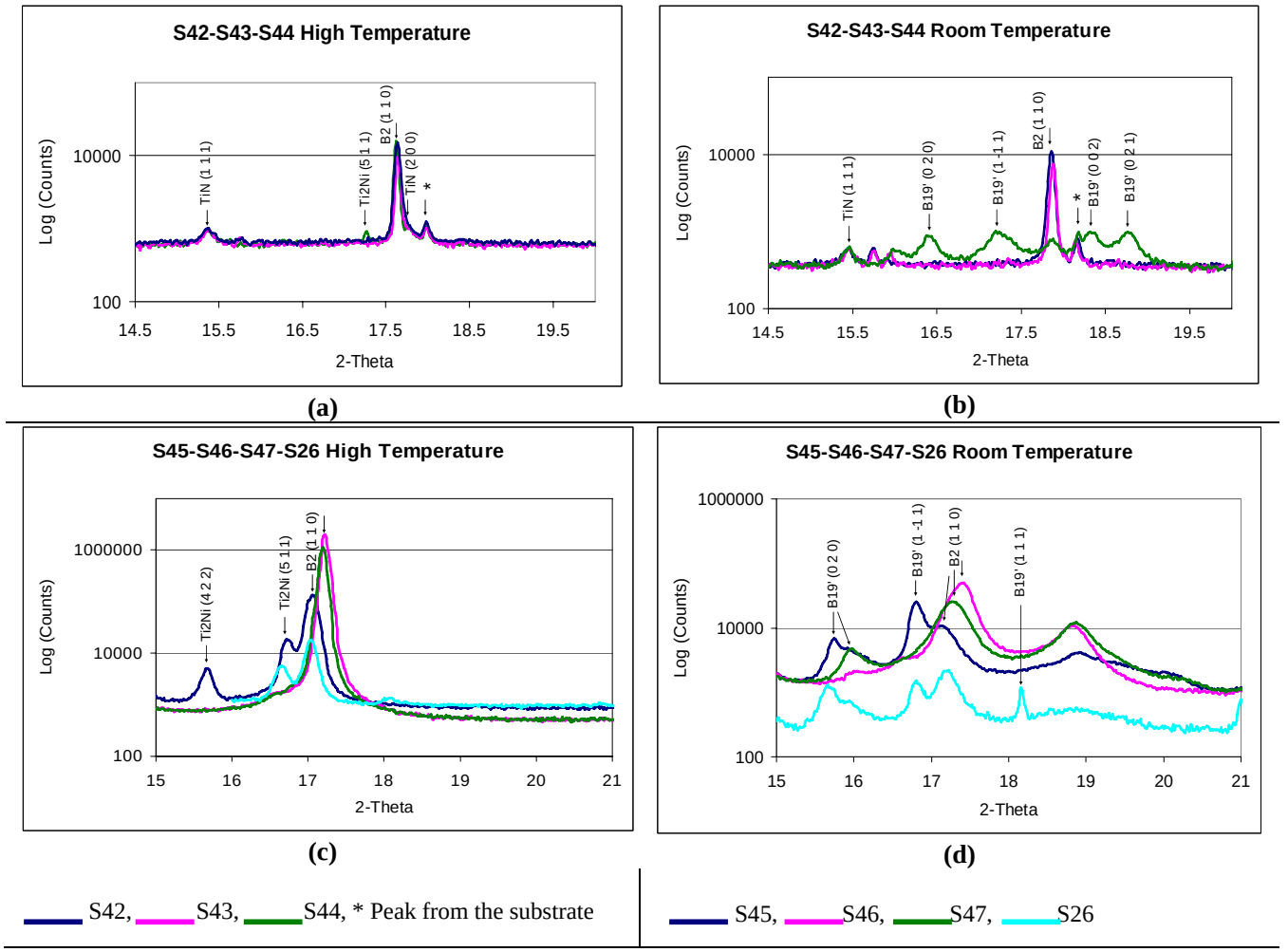


Fig. 3: XRD patterns of samples S-42–S-44 (a, b), and S-45–S-47 compared with S-26 (c, d).

(a) S-42, S-43 and S-44 at 470ºC (deposition temperature) with TiN as the intermediate layer.
(b) S-42, S-43 and S-44 at room temperature again with TiN as the intermediate layer.
(c) S-45, S-46, S-47, and S-26 at 470ºC (deposition temperature) with HfN as the intermediate layer.
(d) S-45, S-46, S-47, and S-26 at room temperature again with HfN as the intermediate layer.

3.2 NiTiHf / HfN

- the high-temperature transformation characteristics of the NiTiHf shape memory alloys give rise to a martensitic transformation during cooling close to 200ºC,
- the increasing amount of Hf incorporated in NiTiHf thin films shifts the B2(110) peak towards lower 2θ (higher d spacing) and decreases its intensity,
- the presence of Ni_4 $(Ti,Hf)_3$ in the NiTiHf thin films was detected.

4. CONCLUSIONS

The results show that the *in-situ* study by XRD / XRR of the deposition of thin films, where important reactions (precipitation phenomena, phase transformations) take place, is a powerful tool for the development of these materials.