ESRF	**Experiment title:** ***In-situ* study during co-sputtering of TiNi-TiN nano-composite thin films (cont)**	**Experiment number:** **MA-105**
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REPORT:

The effect of a TiN layer deposited on top of the SiO_2/Si(100) substrate prior to the deposition of the Ni-Ti films has been analysed in previous experiments [reports ME-1087 and 20_02_637]. Due to the promising results obtained concerning the manipulation of the preferential orientation of the Ni-Ti thin films through the deposition of a TiN buffer layer [1], complementary tests have been performed on this subject. During this beamtime there was also the opportunity to complete a series of methodical investigations on Si(100) substrates.

EXPERIMENTAL

The Ni-Ti films and the TiN buffer layers were deposited by D.C. magnetron sputtering in a chamber especially designed for *in-situ* x-ray measurements [2]. Two unbalanced magnetrons, equipped with a 25.4 mm Ni-Ti target (51 at% Ni – 49 at% Ti) and a 25.4 mm Ti 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 buffer layers, the Ti 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 films the Ni-Ti and Ti magnetrons were driven at a power of 40 and 24 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 deposition	*Ni-Ti deposition*	*TiN*	*Ni-Ti*	*TiN*	*Ni-Ti*
S50	SiO_2^*/Si(100)	TiN	-30	0	32 (at ≈600°C)	123	105 (at ≈600°C)	52
S51	SiO_2^*/Si(100)	TiN	-30	0	3	118	120	58
S53	MgO(100))	TiN	-30	0	3	120	80	54
S52	SiO_2^*/Si(100)	–	–	0	–	134	–	62
S54	Si(100)	–	–	-45	–	122	–	60
S55	Si(100)	–	–	0	–	118	–	54

[*] 1400 Å amorphous SiO_2 capping layer

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

RESULTS AND DISCUSSION

The TiN buffer layer of *sample S50* lead to a preferential growth of {110} Ni-Ti B2 planes parallel to the substrate from the beginning of the deposition with a constant growth rate during the whole deposition (Fig. 1). The diffraction peak B2(211) also appears and grows but with a much lesser intensity. In the case of the B2(200) peak, it was detected later (with low intensity) in contrast to what is observed when the Ni-Ti films are deposited directly on SiO_2/Si(100) substrates [3, 4].

Specular reflectivity (XRR) has been employed to characterize the TiN buffer layer of *sample S51* (Fig. 2). The results did not show evidence of a structural change due to the annealing step. The XRR curves immediately after deposition and 90 min later are superposed.

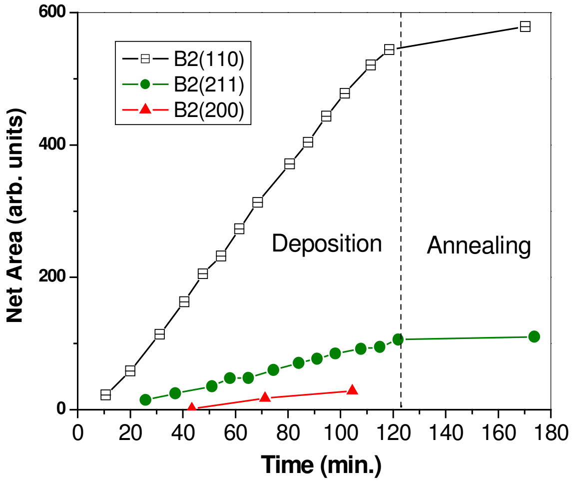

Fig. 1: *Sample S50:* the integrated intensities of the Bragg-Brentano B2(110), B2(211) and B2(200) diffraction peaks as obtained from the positions of the respective peaks, recorded as a function of time after start of film growth.

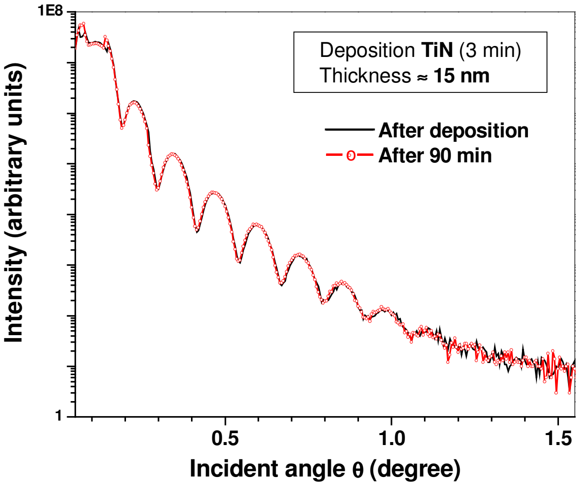

Fig. 2: XRR spectra obtained immediately after deposition and XRR spectra obtained 90 min after deposition of TiN (buffer layer of *sample S51*).

Low angle specular reflectivity time resolved at a fixed incidence angle was as well very useful to determine the growth mode of the TiN buffer layer and the Ni-Ti film (first 9min 30s) for the deposition on MgO(100) substrate (*sample S53*, Fig. 3), revealing a layer-by-layer growth mode (with the decrease in oscillation amplitude, indicating that the surface becomes rougher during sputtering). A single orientation of Ni-Ti is grown during the 120 min of deposition, with (100) stacking parallel to the substrate. The first layers deposited on the TiN (100) are constrained (compressive planar stress state) and this deformation remains until the end of the deposition; later layers are having a gradually relaxed interplanar distance (smaller $d_{(200)}$ in the direction of the surface normal), indicating a gradual relaxation of the compressive stress constraint imposed at the interface Ni-Ti/TiN (Fig. 4).

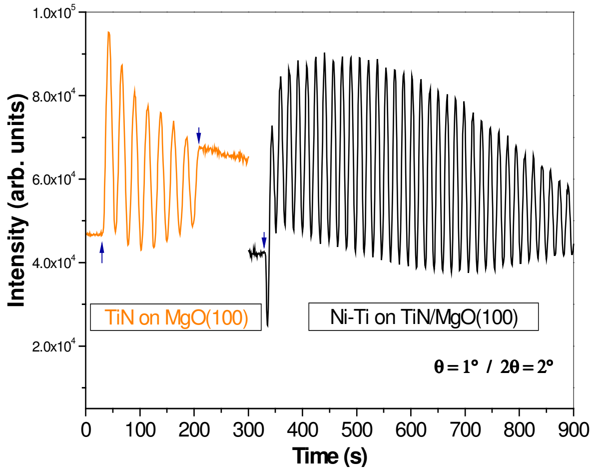

Fig. 3: Time-dependent *in situ* XRR for the TiN buffer layer and the first minutes of deposition of the Ni-Ti film on MgO(100) substrate (*sample S53*).

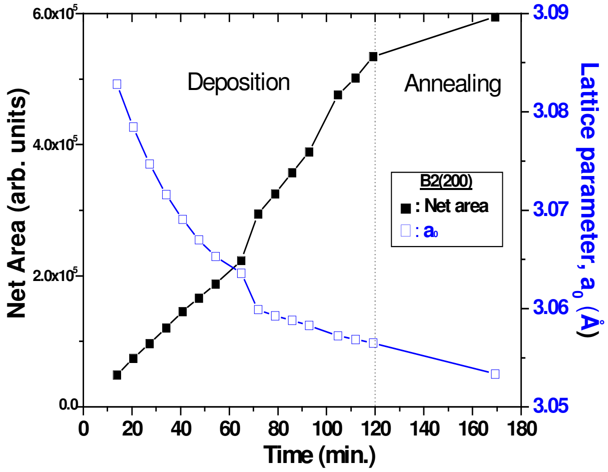

Fig. 4: The integrated intensities of the Bragg-Brentano B2(200) diffraction peak and the lattice parameter a_0 as obtained from the position of the peak, recorded as a function of time after start of Ni-Ti film growth (*sample S53*).

The complementary tests on Si(100) substrates have shown that the use of a substrate bias voltage (-45 V) on naturally oxidized Si(100) (*sample S54*) leads to a film growth where, at the beginning, the {200} planes are stacking parallel to the substrate like for depositions without bias voltage (*sample S55)* [5-8]. However, after the stabilization of the B2(200) intensity there is the development of grains with the {310} planes parallel to the substrate in contrast to the B2(110) preferred orientation observed for depositions without bias. This result confirms the information obtained in a previous experiment using a substrate bias voltage of -25 V [*sample S39*, report 20_02_637].

CONCLUSIONS

- A preferential growth of {110} Ni-Ti B2 planes parallel to the substrate from the beginning of the deposition can be obtained using a TiN buffer layer. In this case the <100> orientation is greatly reduced with the appearance of the B2(200) peak only at a later stage of the Ni-Ti deposition.
- A single orientation of Ni-Ti (≈900 nm) with (100) stacking parallel to the substrate can be produced using a TiN(100) buffer layer. The experiments also show that the TiN layer acts as a diffusion barrier. In contrast to the Ni-Ti film deposited directly on MgO(100) (*sample S24*, [report ME-936]), here no peaks from interfacial reaction products were detected.
- The use of a bias voltage on naturally oxidized Si(100) substrates leads to a dominance of grains of the Ni-Ti B2 phase with the (310) orientation parallel to the substrate after an initial stacking of the B2 phase onto (h00) planes.

References

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