ESRF	**Experiment title:** ***In-situ* study during co-sputtering of NiTi-TiN nanocomposite thin films**	**Experiment number:** **ME-1087**
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Report:

The growth of near-equiatomic NiTi thin films on oxidized silicon wafers, deposited by magnetron co-sputtering from NiTi and Ti targets, has been studied *in situ*. Widening the scope of the previous experiments concerning the influence of the deposition parameters on the film structure [1-4], here the incorporation of TiN at different steps of the NiTi depositions was tested. TiN films grown by vapor phase deposition techniques usually have a preferred growth orientation that varies according to the growth conditions. Previous measurements performed by the ROBL staff were fundamental in choosing the deposition conditions for TiN [5].

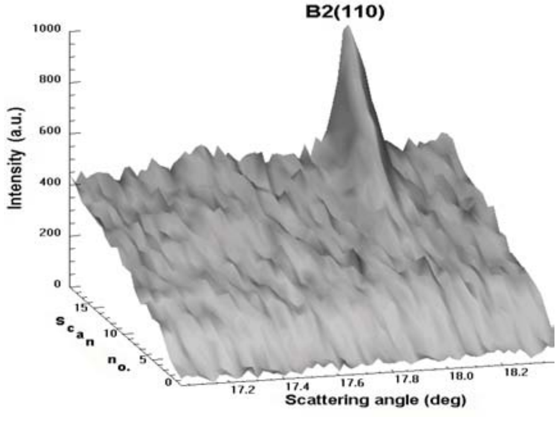
EXPERIMENTAL

The samples were deposited in the sputter chamber installed on the 6-circle-goniometer of ROBL [6]. Pieces of size 15×15 mm^2, cut from Si(100) wafers with a 1400 Å amorphous SiO_2 capping layer, have been used as substrates. The magnetron with the NiTi alloy target (49 at% Ni – 51 at% Ti) was run at a dc power of 40 W. The magnetron with the pure Ti target (99.99 %) was run at 20 W for the NiTi depositions and at 80 W for the TiN (deposition pressure $= 3.5\times10^{-3}$ mbar). The substrate temperature was kept at $\approx$ 470°C. The scans were run in Bragg-Brentano geometry, using 0.675 Å radiation.

Sample	*TiN deposition:* **ratio Ar/N$_2$**	*Substrate bias (V)*		*Deposition (min.)*						*Annealing (min.)*	
		TiN deposition	Ni-Ti *deposition*	*TiN (on top of Si wafer)*	*NiTi 1st layer*	*TiN 1st inter-mediate*	*NiTi 2nd layer*	*TiN 2nd inter-mediate*	*NiTi 3rd layer*	*TiN (on top of Si wafer)*	*After last deposition of NiTi*
S29	-	-	-45	-	128	-	-	-	-	-	83
S30	9.4/4.7	-30	0	50	120	-	-	-	-	131	113
S31	10/2.5	-30	0	40	122	-	-	-	-	27	57
S32	10/2.5	-30	0	15	120	-	-	-	-	28	60
S33	10/2.5	-30	0	3	60	0.5	60	-	-	87	77
S34	10/2.5	-30	0	3	122	-	-	-	-	27	60
S35	10/2.5	-30	0	3	40	1	40	3	40	105	62

Deposition parameters for the various samples investigated.

RESULTS



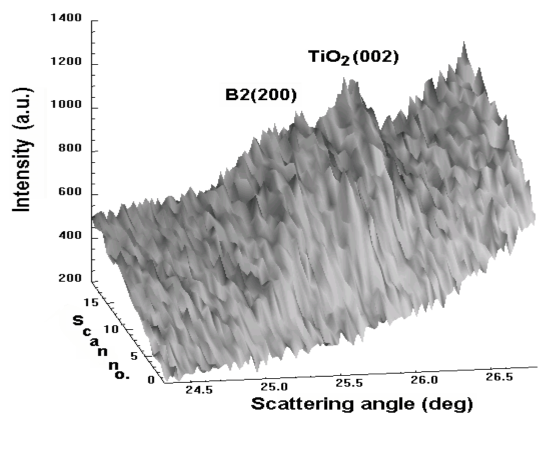
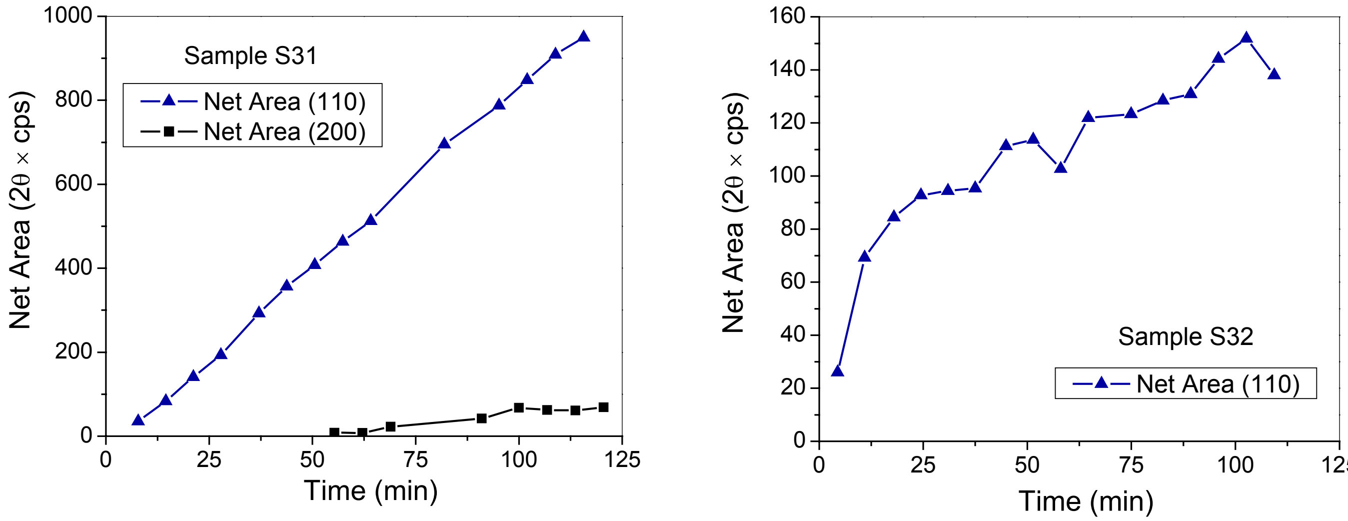


Fig. 1: XRD spectra with peak evolution during the deposition of sample S29.



(a) (b)

Fig. 2: Evolution of the net area of the diffraction peaks B2(110) and B2(200) for sample S31 (a), and for the diffraction peak B2(110) for sample S32 (b) during deposition.

Sample S33

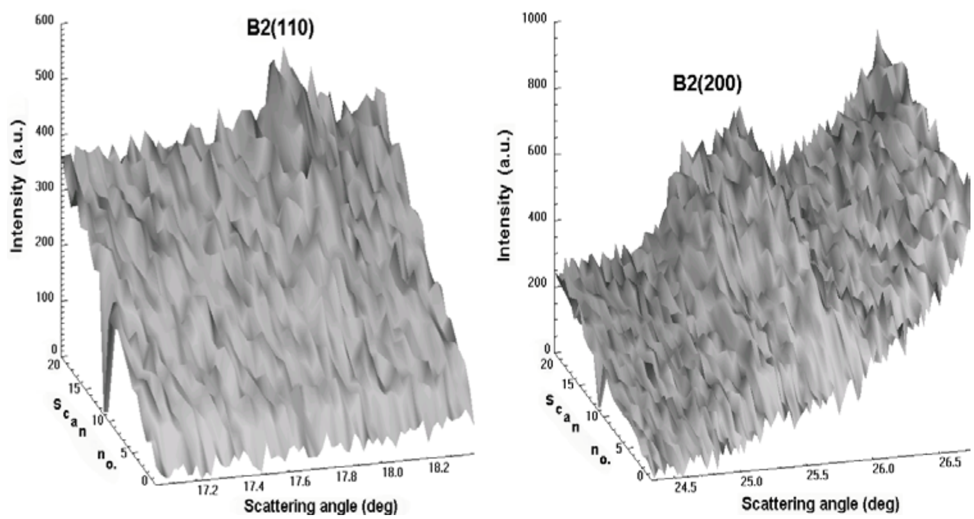


Fig. 3: 3D plots of the peak intensity of B2 phase [left: B2(110), right: B2(200)] of samples S33 (top part) and S34 (bottom part).

Sample S34

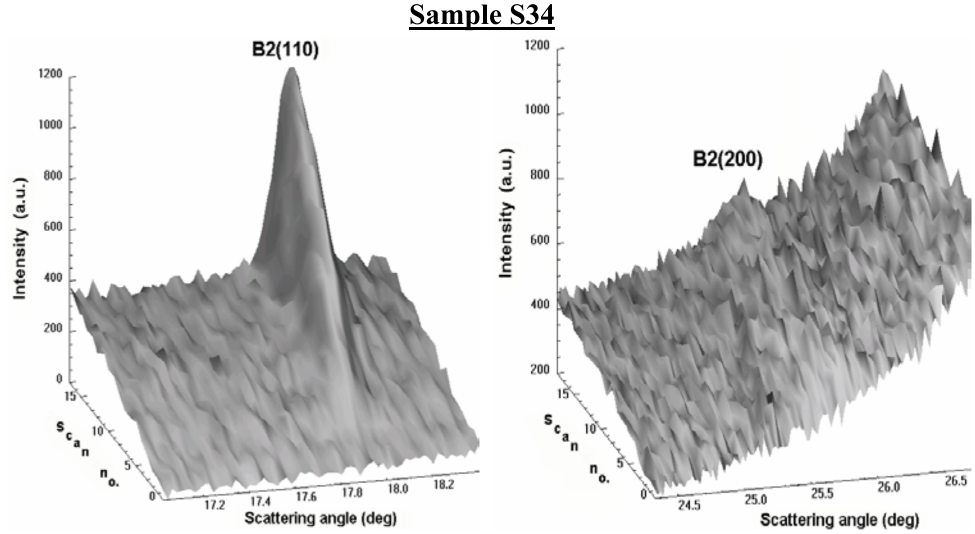
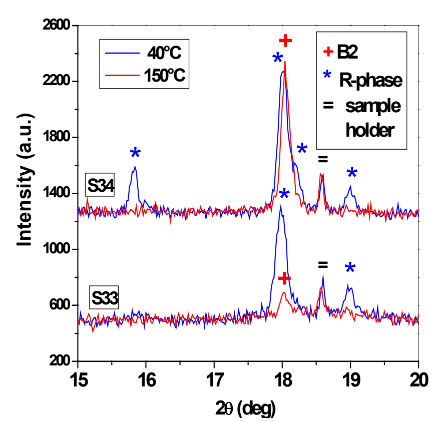


Fig. 4: Crystalline structure changes of NiTi films S33 (bottom) and S34 (top) at different temperatures. ∇



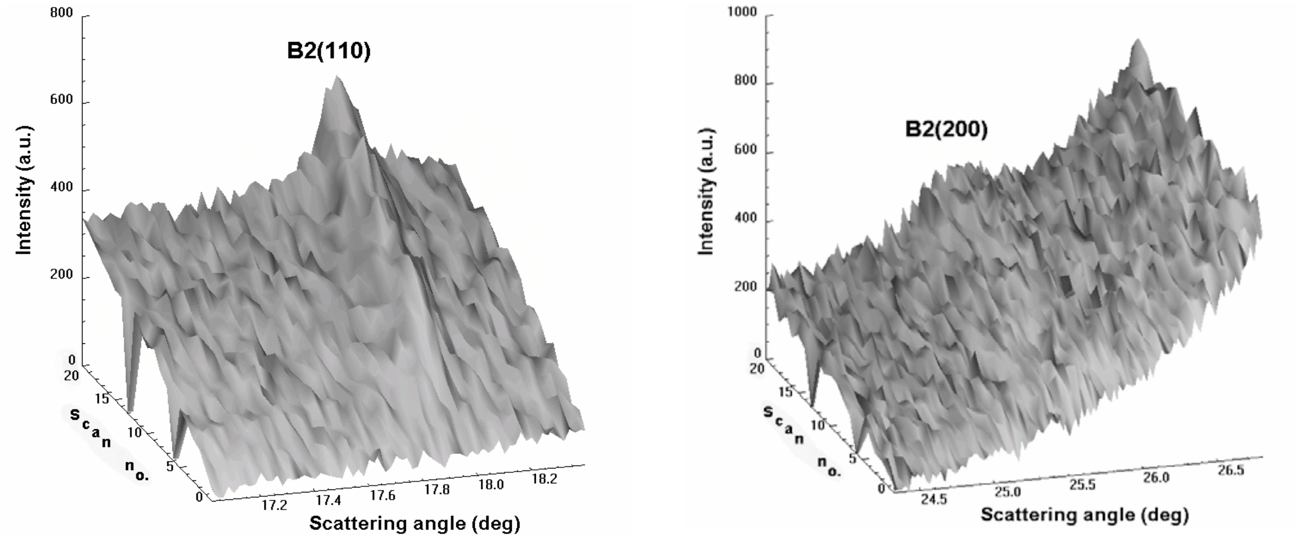


Fig. 5: 3D sequence of XRD patterns of sample S35 during deposition.

Note: The zero intensities are manually inserted into the graphs to mark the last scan during the deposition of NiTi before a deposition of an intermediate layer of TiN (scans during the deposition of TiN are not represented).

The type of substrate plays an important role for the preferential stacking of sputtered NiTi films. Previous experiments with deposition on Si(100) have put in evidence that B2 phase starts by stacking onto (100) planes and, as the thickness increases, the preferred orientation changes to (110) fiber texture. However, for NiTi films deposited on Si substrates at high temperatures, there exist interfacial diffusion and chemical interactions at the interface resulting in silicide formation. During experiment ME-936 a SiO_2 layer was used as an effective barrier. There, a preferential stacking of B2(100) was observed when using a Si oxidized substrate (*no* bias). We suggest that a stronger interfacial adsorption on the heated substrate promotes the preferential coverage by a first layer of Ti on top of the SiO_2/Si substrate. This leads to the preferential formation of the (h00)-oriented NiTi film since, in the B2 cubic structure, the (h00) planes are alternately occupied by Ni and Ti atoms.
In the present experiments, the bias effect was studied (sample S29). During the deposition, the first deposited layers had a (100) orientation, later changing into (110) (Fig. 1). We consider that the more energetic ion bombardment of the growing film enhances the surface mobility of Ni and Ti adatoms, inducing the fiber texture (110), which is the more densely packed crystallographic plane. Apparently, due to the existence of a large amount of oxygen on the SiO_2 layer, Ti atoms arriving on the SiO_2 surface get oxidized, forming a thin interfacial layer of TiO_2. The deposition of TiN was then tested as a possible future tool to control the properties of this type of films to be used for the functional devices.
The results have shown that TiN acts not only as a diffusion barrier, but also induces different crystallographic orientations depending on the process conditions like deposition parameters or annealing time:
- in sample S31 (Fig. 2-a), the TiN layer induces the preferential growth of (110) plane parallel to the substrate from the beginning of the deposition, with a constant rate up to the end of the deposition; the diffraction peak (200) appears only at a later stage, always remaining very weak;
- for the sample S32, the diffraction peak (110) also appears since the beginning of the deposition (though much less intense); at the end of the deposition, still there is no evidence of the (200) diffraction peak (Fig. 2-b);
- samples S33-S35 (Figs 3-5) are characterized by different preferential orientations; Fig. 4 shows that, in the case of samples deposited on the top of an intermediate TiN layer, the R-phase transformation is detected while cooling.

CONCLUSIONS

These experiments have proved the usefulness of the TiN layer as (i) an efficient diffusion barrier and (ii) to induce different preferential orientations of the growing film. Further studies are required to clarify the role of TiN deposited as an intermediate layer on top of a Si substrate or during the NiTi deposition. This will help to define the parameters in order to use TiN to manipulate the texture of NiTi films. This is very important because the recoverable strain depends on the texture and strong textures may lead to anisotropic shape memory behavior.

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