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Growth, microstructure and thermal transformation behaviour of epitaxial Ni-Ti films

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ABSTRACT

Epitaxial films have the potential to be used as model systems for fundamental investigations on the martensitic transformation in binary NiTi. In this paper, we discuss growth of binary NiTi thin films on single crystalline MgO substrates. Sputter deposition is used to grow NiTi films. Films prepared by complementary preparation routes (with different deposition temperatures and subsequent heat treatments) are investigated by X-ray diffraction, electron microscopy, atomic force microscopy, and electrical resistivity measurements, with the aim of optimizing film properties, particularly to obtain a well defined orientation of the austenitic unit cell and smooth surfaces. Our results show that deposition at elevated temperatures and carefully controlled subsequent heat treatments allow to produce epitaxially grown and smooth NiTi films that exhibit reversible one- or two-step martensitic transformations.

1. Introduction

Epitaxial films are model systems that can be used for fundamental investigations which allow for a better understanding of shape memory alloys (SMA). This idea has been extensively applied to research on magnetic shape memory alloys where epitaxial films have helped to measure the electronic origin of the martensitic transformation [1], determine twin boundary energies [2], examine hierarchically twinned microstructures [3], and demonstrate the adaptive nature of modulated martensite [4]. Most of these research efforts have simply been a by-product of the need for epitaxial films for microactuators [5], which represent the thin film counterpart of single crystals and which are required to reach the highest strains in magnetic shape memory alloys.

In contrast NiTi, the first and most important technologically applied shape memory alloy, can be used as polycrystalline material. A good summary on polycrystalline SMA films can be found in the textbook of Miyazaki [6]. Most common techniques are DC magnetron sputter deposition [7], co-sputter deposition [8], molecular beam epitaxy [9] or biased target ion beam deposition [10]. Typically, polycrystalline films are deposited onto amorphous and/or oxidized substrates such as Si_2O or Si and subsequently annealed [11–13]. So far only a few studies have examined the epitaxial growth of NiTi films on heated substrates [9,14]. One open research question is if epitaxial NiTi films can be used to contribute to a more fundamental understanding of the basic behaviour of NiTi SMA, as sketched above for magnetic SMA. Moreover, epitaxial NiTi films might even improve the functionality compared to polycrystalline NiTi films, which have already been developed towards microactuators [15], stents for brain surgery [16], elastocaloric refrigeration [17], or used for the combinatorial search for low hysteresis materials [18,19].

Fundamental as well as applied research on epitaxial NiTi films will benefit from two main aspects, both of which we address in this paper: First, a well-defined orientation of the austenitic unit cell in the epitaxial films is required. This allows probing anisotropic properties and identifying orientations within the martensitic microstructure after cooling. Second, a smooth film surface is essential, as only such a well-defined cut through the crystal allows distinguishing a martensitic microstructure from film morphology later on. Small scale mechanical testing also requires smooth

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surfaces to avoid crack formation in tensile tests [20] or adverse effects on nanoindentation measurements [21,22]. Both aspects can be examined best when the film is within the austenitic state at room temperature and therefore in the present study we focus on a film composition where the martensitic transformation occurs just below room temperature. We compare three different preparation routes: **A** depositing at room temperature followed by annealing; **B** depositing at high temperatures; **C** depositing at a moderate temperature followed by an annealing and temper step, and we investigate their effect on microstructures, surface features and thermal transformation behaviour in the resulting epitaxial NiTi films.

2. Experimental

Physical vapour deposition based on a DC magnetron sputtering process was used with a $Ni_{46.8}$ $Ti_{53.2}$ alloyed target for deposition at different temperatures. The base pressure was lower than $<10^{-8}$ mbar. A mixture of argon and hydrogen was used as protective atmosphere and a sputter power of 100 W was applied. In order to induce an epitaxial growth of the deposited NiTi films we used single crystalline MgO(001) substrates. The films were grown to a thickness of 120 nm at an average growth rate of 0.16 nm/s.

In this study we systematically discuss results for three main preparation routes: In a first series, films were deposited at room temperature. Subsequently, the films were annealed in the deposition chamber between 450° C and 850° C for different times to promote thin film crystallization. This preparation route is referred to hereafter as route **A**. In a second series (route **B**), substrate temperatures between 150 and 650° C were used in order to enable epitaxial growth and chemical ordering during the deposition process itself. For the third series (route **C**), films were deposited at 250° C and subsequently annealed. An additional tempering at 300° C for 20 min was applied. All annealing and tempering steps were performed in-situ in the deposition chamber with a base pressure of 10^{-7} mbar. In order to suppress decomposition of the NiTi films, two step cooling with cooling rates faster than $r > 50\,^{\circ}C/min$ were applied. The heater was immediately switched off once the heat treatment was finished. For subsequent cooling, the samples were then transferred into a cool pre-vacuum chamber with a base pressure of (10^{-6} mbar). The composition of all films was determined as about $Ni_{50.1}$ $Ti_{49.9}$ (±0.1 *at %*). Comparing target and thin film compositions, we note a loss of Ti during deposition, which is a well-known effect [7].

The following analytical methods were used to characterise the chemical composition, microstructure and topography of the samples: For energy dispersive X-Ray spectroscopy (EDX) measurements, a Philips scanning electron microscope (SEM) with a Ni_{50} Ti_{50} standard was used. Phase analysis was carried out using X-ray diffraction (XRD) in a Bruker D8 X-Ray diffractometer with Co-K_α radiation. To analyse global textures, pole figures were measured using a four circle set-up (Philips X'Pert) in the range of $0° \leq \varphi \leq 360°$ and $\psi \leq 80°$ in steps of 1° with Cu-K_α radiation. Based on the pole figure measurement results, complementary local texture measurements were performed by electron backscatter diffraction (EBSD) with a NEON40EsB (Zeiss) SEM. Sample surfaces were examined using a DI Dimension 3100 atomic force microscope (AFM) in tapping mode. Data analysis was performed using the freely available WSxM software [23] and root mean square roughness (RMS) values were determined from $20 \times 20\ \mu m^2$ areas. Finally, in order to directly evaluate the thermal transformation behaviour, temperature dependent electrical resistivity measurements were performed in four-contact geometry using a Quantum Design Physical Properties Measurement System (PPMS).

3. Results

3.1. Room temperature deposition and post-annealing - route *A*

Similar to already reported studies on silicon substrates [6], our observations show that NiTi films deposited at room temperature on single crystalline MgO(001) substrates also exhibit amorphous structures. We therefore selected annealing temperatures between 450° C and 850° C, close to those reported in the literature. Annealing times were selected as 60 and 120 min, respectively.

Fig. 1a shows selected XRD scans in θ-2θ geometry for different annealing temperatures ϑ_A and an annealing time of 120 min. For the as-deposited film ($\vartheta_D = 30\,^{\circ}C$) no NiTi reflections are observed due to the amorphous structure. Annealing between 450° C and 650° C leads to crystallization in the B2 phase, as indicated by the $(001)_{B2}$, $(002)_{B2}$ and $(211)_{B2}$ reflections. Furthermore, a splitting of the $(001)_{B2}$ reflection is observed, which is usually discussed as the formation of *R*-Phase via a martensitic transformation where the B2 austenite cell is subjected to a rhombohedral distortion [24]. A more detailed discussion on the observed peak splitting is given below (section 3.2). When increasing annealing temperature to 850° C, the intensity of the $(002)_{B2}$ reflection decreases and other reflections close to $(211)_{B2}$ and $(111)_{B2}$ increase. This confirms that the polycrystalline film growth occur mainly with a $(211)_{B2}$ orientation. Beside reflections originating from the B2 phase minor reflections are observed on the logarithmic scale. These reflections may well be associated with the onset of the formation of oxides. Such thin oxide layers can be formed during annealing within a sputter chamber [25].

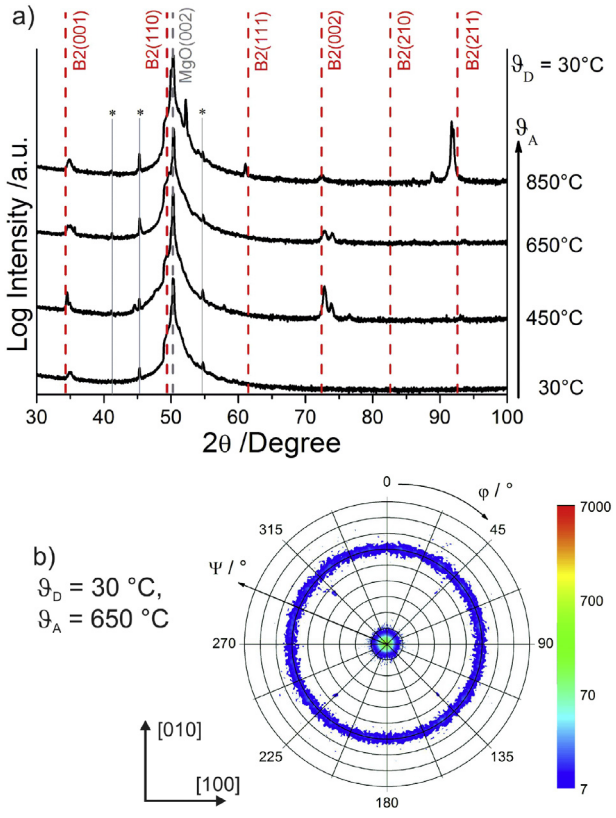

Fig. 1. Route **A**: (a) Image section of the measured XRD θ-2θ scans of NiTi films on MgO(001) substrates deposited at $\vartheta_D = 30\,^{\circ}C$ and annealed at different temperatures ϑ_A. Dashed lines mark the reflection positions of bulk Ni-Ti *B2*. Reflections marks by stars arises from the XRD set-up. (b) Typical $\{101\}_{B2}$ pole figure measured of the film deposited at $\vartheta_D = 30\,^{\circ}C$ and annealed at $\vartheta_A = 650\,^{\circ}C$.