Epitaxial Fe-Pd Magnetic Shape Memory Films - Issues for Preparation and Applications

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Abstract:
For the MSM effect in disordered Fe-Pd films, epitaxial, and thus single-crystal-like films that exhibit the metastable fct martensite are anticipated. Within the DFG SPP-1239, our project “Extrinsic properties of epitaxial Fe-Pd MSM films” is part of a joint collaboration “Fe-Pd-X Thin Film-Polymer Composites for Sensor Applications” aiming at new magnetic shape memory Fe-Pd-X films for sensor applications. The goal is to prepare Fe-Pd magnetic shape memory films with good extrinsic properties, especially a low actuation field and a strain suitable for sensor applications. Films are prepared using pulsed laser deposition. Epitaxial growth, phases, microstructure and magnetic properties are examined in dependence of film composition. Film stress causes the occurrence of stress induced martensite. Freestanding Fe-Pd films are prepared by substrate etching.

Keywords: magnetic shape memory, epitaxy, films, Fe-Pd

Introduction
Fe-Pd [i] is a competing Magnetic Shape Memory (MSM) material to Ni-Mn-Ga. At low temperatures Fe-Pd can reach a strain up to several percent [ii], comparable to the 6 % strain reached in 5M modulated Ni-Mn-Ga [iii], but less than the 10 % strain reached in 7M modulated Ni-Mn-Ga [iv]. In our recent publications we discussed structure, microstructure and magnetic properties of epitaxial Fe-Pd films including the experimental details and give an overview on film preparation and structure [v] and the magnetic properties of Fe-Pd films [vi] [vii]. In the following paper we give a comprehensive overview of our results.

Results
Investigations were performed on disordered Fe-Pd films deposited on MgO (100) single crystalline substrates by PLD at room-temperature. If not stated differently the films nominal thickness is 300 nm.

a) Structure and Microstructure
Structural characterization of as-deposited films by X-ray diffraction (Fig. 1) [v] shows formation of bcc, bct and fct phases with increasing Pd content. Compared to bulk FePd, the fct-phase occurs in a strongly composition expanded range from 29 to 43 at.% Pd in pulsed laser deposited films (Fig. 2). The measured tetragonal distortion of the bct phase with c/a > 1 and the fct phase with c/a < 1 agrees with literature [viii]. Bcc exhibits c/a = 1 (Fig. 2). The fcc phase is not observed. The XRD coherence length of fct is as low as 3 nm, indicating very small grain or variant size.

The c - axis of the fct phase is aligned in-plane since only the (200) reflection is observed in XRD. This indicates that only two variants occur in the films, no third variant with the c-axis oriented perpendicular to the film plane is observed. Pole figure measurements, prove epitaxial film growth (Fig. 2 inset). For fct-films thicker than 20 nm (111) deformation twins were observed. Due to the deformation twinning, a (111) reflection appears in XRD (Fig. 2). The measured tetragonal distortion of the bct phase with c/a > 1 and the fct phase with c/a < 1 agrees with literature [viii]. Bcc exhibits c/a = 1 (Fig. 2). The fcc phase is not observed. The XRD coherence length of fct is as low as 3 nm, indicating very small grain or variant size.

Fig. 1: Composition dependent phase formation observed in XRD (Co K,)

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b) Film Stress and Consequences

We proposed in [v] that both, stabilization of the fct phase, and the (111) twinned microstructure are caused by film stress. In-situ stress measurements were performed during PLD of pure Fe and Fe-Pd films with 20, 30 and 40 at.% Pd, respectively [ix]. Both films with bcc structure (pure Fe and Fe-Pd with 20 at.% Pd) exhibit compressive film stress throughout the film growth. Compressive stress is typical for PLD films [x], [xi] and can be explained by shoot-peening due to high energy ions [xii]. In contrast to bcc films growth, during fct film growth, tensile stress is observed initially. This tensile stress can be explained by the mismatch to the substrate which dominates the film stress state during the initial stages of fct-film growth. Whereas bcc films exhibit a low mismatch to the MgO substrate, fct films have a significant mismatch of -9% for the a-axis and -12% for the c-axis, leading to the observed initial tensile stress.

At a film thickness of 20-25 nm, the same thickness at which the onset of (111) twinning has been observed by XRD and pole figure measurements, relaxation of tensile stress and a pronounced change to compressive film stress was observed [8]. This suggests that the (111) twinning causes relaxation of initial tensile film stress. The (111) twinning does not occur at smaller film thickness, since it is suppressed by the interface to the substrate.

When the fct film thickness exceeds 20-25 nm, compressive stress is observed, which can again be explained by the atomic-peening during PLD. The observed high stress in fct-films can explain the stabilization of the fct-phase and in addition why no variant with the c-axis perpendicular to the film plane is observed. According to the mismatch only, the alignment of the unit cells with only a-axes in-plane (and the c-axis out-of-plane) should be preferred. This would result in a single variant film growth that cannot accommodate stress by twinning. On the contrary, introduction of martensitic (110) twin boundaries costs relatively little energy. When the c-axis lies in plane, the relaxation of the films by splitting up into variants is possible. This is thus a very efficient way to reduce the film stress, causing that the a-axis alignment normal to the film plane, despite the higher misfit, is more favourable for the system.

c) Magnetic Properties and Magnetic Identification of Phase Transitions

For MSM materials studies of the magnetic properties and their dependence on film structure are essential for applications. The stress induced stabilization of the fct-phase allows investigation in a wider composition range compared to bulk, e.g. the magnetic properties of fct could be investigated up to an “unnaturally” high Pd content.

Magnetic properties of the as deposited films have been investigated in dependence of film composition and temperature. The magnetic properties at room-temperature and at low temperatures have been interpreted with regard to structure and microstructure and are discussed in comparison to supporting DFT calculations [vi]. According to the DFT calculations, decreasing c/a ratio (increasing tetragonal distortion) and increasing Pd content (increasing band filling) have a similar effect,
leading to an increase of the magnetic anisotropy energy (MAE). At room temperature, the shape of the hysteresis loop differs for bcc/bct films in comparison to fct films (Fig. 3). Bcc and bct films exhibit low coercivity and the step-like shape of the hysteresis suggests low magnetocrystalline anisotropy. In contrast, the hysteresis curves measured for fct films exhibit a strongly increased coercivity and saturate at higher fields, indicating increased magnetocrystalline anisotropy. With increasing Pd content in the fct films, coercivity and magnetic anisotropy energy increase. However, in comparison to bulk fct Fe-Pd, the absolute MAE in the fct films is reduced. This can be explained by the random anisotropy model [xiii] which needs to be considered for the nanoscaled microstructure in the films, as well as by the misoriented growth.

![Fig. 4: Temperature dependence of saturation field and coercivity for different compositions extracted from hysteresis measurements](image)

Magnetic measurements have also been performed at low temperatures, the results are published in [3]. For fct films with a composition close to 30 at.% Pd, the hysteresis show a gradual decrease of coercivity and saturation field (as a measure for the magnetic anisotropy energy) with decreasing temperature which can not be explained by the behaviour of an ordinary ferromagnet and indicates a phase transition (Fig. 4). The measured temperature- and composition-dependent change of coercivity and saturation field was compared to the characteristic hysteresis curves of the different phases at room temperature and the “metastable phase diagrams” published in literature[xiv], [xv]. Accordingly this phase transition can be identified as fct-bct phase transition. The gradual change of the magnetic properties indicates a continuous formation of the bct phase with decreasing temperature. In Fe-Pd bulk material, the occurrence of the bct-martensite at low temperatures irreversibly destroys the MSM effect. In contrast to bulk, where this phase transition is irreversible due to the significant volume change involved, it is found to be reversible in thin films. The reason for this is the additional free dimension in thin films: a length change to accommodate the volume change is easily possible in the out-of-plane direction. This reversibility might be an important advantage for future Fe-Pd film applications.

d) Film Stability at Elevated Temperatures

In order to examine the stability of fct-phase and the chemical stability of the films, the magnetic behaviour of fct-films at elevated temperatures was studied. The results are published in [vii]. Magnetic hysteresis loops of fct films with 33 at.% Pd have been measured up to 600 K. No indication of an fct-fcc phase transition was observed. This implies an increased stability of the fct phase in the films, which is in agreement with the severe film stress stabilizing the fct-phase.

The investigated, disordered Fe-Pd alloys are metastable. So far, in previous measurements at elevated temperatures, decomposition of the fct films has been avoided by the choice of appropriate conditions (fast measurements, limited temperature). Decomposition can, however, become important during applications at elevated temperatures as well as temperature dependent magnetization measurements. This has been shown for a sample with lower Pd content that was exposed to higher temperatures for longer times in comparison to the previously discussed measurements. Decomposition of the bcc disordered phase into Fe-rich and L10 equilibrium (stable) phases was observed to begin at 560 K and leads to a gradual decrease of magnetization with increasing temperature in temperature dependent measurements (instead of a sharp reduction as expected at the Curie temperature TC). Furthermore irreversible behaviour was observed. The formation of the L10 phase by decomposition with its high magnetocrystalline anisotropy was confirmed by hysteresis measurements, showing increase of coercivity with annealing time.

d) Routes to Free Standing Films

However, since the MSM effect can only produce stress in the range of a few MPa, freestanding films are needed which are not constrained by the substrate. Since MgO substrates, selected due to its inert behaviour during film deposition, can not be etched chemically selectively, other releasing methods are required for the preparation of freestanding films. It has been demonstrated that non-transparent films on a transparent substrate can be released by shooting laser pulses through the substrate on the backside of the films, leading to a
film lift-off by local evaporation of film material at the film-substrate interface [xvi]. According to this, Fe\textsubscript{70}Pd\textsubscript{30} films were prepared on 150 \textmu m thin, double-side polished MgO(100) substrates. By directly irradiating the front side of the Fe-Pd film, the energy threshold for evaporation of 0.50 J/cm\textsuperscript{2} was determined. Considering absorption by the substrate itself, 0.64 J/cm\textsuperscript{2} were applied for the back-side irradiation through the MgO substrate. Since no homogeneous release of the film could be achieved, thus this approach is not useful for releasing.

An alternative are Si substrates that are favourable for the integration into real sensor-systems, and, in addition, can be etched relatively easy. For these reasons, Si substrates have been tested as substrates for laser deposited Fe-Pd films. A polycrystalline Fe-Pd film could be released by substrate etching using the TMAH etchant (Fig. 5) and shows foil like behaviour and good mechanical strength despite its low thickness of only 300 nm.

![Fig. 5: SEM of a freestanding film (30 at.% Pd) put on a carrier-substrate](image)

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**References**


