Substrate-free structures of iron-doped Ni-Mn-Ga thin films prepared by pulsed laser deposition

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Abstract. We discuss the preparation of thin films of ferromagnetic shape-memory Ni-Mn-Ga alloys on NaCl using pulsed laser deposition and present a simple way to release the film from its substrate and to realize free-standing Ni-Mn-Ga structures.

1. Introduction
Ferromagnetic shape-memory (FSM) materials are promising candidates for various actuator and sensor applications due to their large strains and shape changes in an external magnetic field [1,2]. The phenomenon is based on the martensitic transformation of the crystal lattice below a certain temperature and the rearrangement of the martensitic twin variants in the magnetic field. The largest magnetostrains, up to 10 %, have been observed in Ni-Mn-Ga alloys [3,4]. In addition, the magnetic, magnetoelastic, and structural properties of these alloys can be tailored by varying the Ni/Mn/Ga composition or by doping the alloy with some ferromagnetic element, e.g., with iron [5–8].

Ni-Mn-Ga has been extensively studied in bulk form. Recently, thin FSM films have also attracted research interest since they allow realizing small micromechanical structures. Furthermore, free-standing Ni-Mn-Ga films are predicted to show a large work output, which is an advantage in future actuators for microelectromechanical systems. [9]

The preparation of Ni-Mn-Ga films has been studied by using, e.g., molecular beam epitaxy (MBE) [9–11], magnetron sputtering [12,13], and pulsed laser deposition (PLD) [14–16]. Typically, semiconductor materials such as silicon and GaAs have been used as substrates but FSM films have also been deposited on μm-thick pieces of poly-vinyl-alcohol which can be dissolved away with hot water [13]. The physical properties of the deposited films have been comparable to those of the best bulk samples and, furthermore, the thermally-induced shape-memory effect and even signs of the FSM effect have been observed in lithographically released films [9].

We have started to systematically study the effect of iron doping on the magnetization, the martensitic phase-transformation temperature, and the Curie temperature of Ni-Mn-Ga films produced by PLD. So far, the films have been deposited on silicon but due to the elastic constraint set by the substrate, neither the martensitic transformation nor the FSM effect has taken place. To eliminate this restriction, we have concentrated on finding better substrate materials which are chemically inert and have a proper lattice match with Ni-Mn-Ga. Currently, the best candidate material is NaCl which has the added advantage that the film can be released from the substrate by simple isotropic etching with water. This makes it possible to study the physical properties of sole Ni-Mn-Ga films. In this article,
we discuss the deposition of Ni-Mn-Ga films on NaCl and demonstrate the realization of free-standing films and small structures.

2. Experimental
The films were deposited on 0.5–1-cm² NaCl (1 0 0) substrates by using the PLD system described in detail elsewhere [17]. The 30-ns-long pulses from a KrF excimer laser were spatially shaped and imaged on the target surface such that the laser fluence was approximately 2.5–3 J/cm². With 40,000 pulses, the film thickness was typically 200–300 nm. The target was a 30-mm-diameter and 3-mm-thick slice cut from a Ni-Mn-Ga ingot [16]. A small notch was cut in the target and an iron wedge was tightly pressed into it. As a result, the iron content of the film can be selected between 0 and 4% because it depends on the radial position of the laser spot on the rotating target. In these experiments, the Fe content was ~ 3%. The depositions were carried out in vacuum (base pressure < 10⁻⁶ mbar), and the substrates were heated to approximately 500 °C. The surface morphology of the deposited films was studied by using a LEO 1450 scanning electron microscope (SEM), their crystal structure was analyzed by a Phillips X'pert X-ray diffractometer, and the magnetization curves were measured with a vibrating sample magnetometer (VSM).

3. Results
The magnetization curve of one of the Ni-Mn-Ga films is shown in figure 1 both with and without the NaCl substrate. Between the two measurements, the sample was gently laid upside down on a piece of flexible plastic and the substrate was removed with water. The curves were measured at room temperature by applying the magnetic field parallel to the film plane; in this direction, the effect of the demagnetizing field on the field inside the sample is negligible. By using the approximate film thickness of 200 nm, a sample area of 0.15 cm², and the bulk density of Ni-Mn-Ga (8 g/cm³), we obtained a saturation magnetization of 42 emu/g. This value is almost 70% of the bulk value and comparable to the saturation magnetizations determined for films deposited on Si [16]. The magnetization remained at this high level even after the substrate was dissolved away.

Figure 2 shows the in-plane magnetization curves for another released film at room temperature, at −50 °C, and at −75 °C. As expected, the saturation magnetization increases by almost 20% as the temperature is lowered and the hysteresis loop becomes wider. According to these results, the sample remains in the austenitic phase at least down to −75 °C. The lattice constant of this phase at room temperature was determined to be 0.580 nm. X-ray measurements also indicate that the film is polycrystalline with a strong (1 0 0) texture in the direction perpendicular to the surface (see figure 3).

![Figure 1](image1.png)  
Figure 1. Magnetization curves of a Ni-Mn-Ga film measured with (full circles) and without (open circles) the NaCl substrate.

![Figure 2](image2.png)  
Figure 2. In-plane magnetization curves of a released Ni-Mn-Ga film at 25 °C (open squares), −50 °C (full circles), and −75 °C (open circles).
To measure the magnetization as a function of temperature, i.e., the $M(T)$ curve, the samples were inserted in a flow cryostat, where the temperature was decreased by adjusting the flow of cold nitrogen gas. The magnetic field had a constant flux density of 0.5 T. The decrease of magnetization at low temperatures (see figure 4) suggests a transformation to a phase with a high magnetic anisotropy, most probably the martensitic phase. Figure 4 shows the $M(T)$ curve for a sample, whose edge was partially released from the substrate within a 1-mm² region to create a Ni-Mn-Ga cantilever. Although the martensitic transformation seems to be gradual and the resulting phase appears not to be fully stable (as evidenced by the peak close to −80 °C), these results support the assumption that shape-memory effects are possible when the substrate does not set restrictions to them. The magnetization seems to decrease as the temperature increases, and provided that it behaves similarly to the magnetization of a typical ferromagnetic material, we can estimate the Curie temperature of the film to be $\approx 120–150$ °C. This is in agreement with the values determined for bulk alloys.

![Figure 3](image1.png) **Figure 3.** Pole figure of a Ni-Mn-Ga film indicates a strong texture in the (1 0 0) direction perpendicular to the surface.

![Figure 4](image2.png) **Figure 4.** Magnetization of a partially released Ni-Mn-Ga film as a function of temperature from −110 °C to +80 °C. The flux density had a constant value of 0.5 T. At low temperatures the continuous decrease of magnetization is a sign of a martensitic transformation.

Figure 5 presents a SEM image of one of the deposited films. The surface is uneven and resembles corrugated iron, most probably because of the large difference in thermal expansion coefficients of Ni-Mn-Ga and NaCl. As the film deposited at 500 °C is cooled to room temperature, the substrate shrinks more than the film and, thus, a small mechanical shock can detach them from each other and produce a wrinkled surface. Only a few droplets can be observed in the dark valleys between the bright hills, which indicates that the deposition parameters used in these experiments were properly selected.

Figure 6 shows a microscope image of a free-standing air-bridge structure fabricated by using UV lithography and isotropic etching with water. The $1000 \times 100$-µm² film-free areas (labeled NaCl in the figure) were created by removing the Ni-Mn-Ga layer with a single diffractively-homogenized excimer-laser pulse (fluence 0.5–1 J/cm²), which passed through a slit-shaped mask. After each shot, the film was translated at 500-µm steps in one of the transversal directions. A few drops of water were applied in the grooves to release the film from its substrate. Due to its macroscopic size and large mass, the bridge typically fell down after the water had evaporated and, in most cases, cracked into two cantilevers as can be also noticed in figure 6. This problem should be easy to eliminate in future experiments by using smaller feature sizes but even these preliminary tests show the potential of this technique in creating µm-sized FSM structures.

4. Discussion
We have studied the pulsed laser deposition of Ni-Mn-Ga thin films on NaCl and released the deposited films from their substrates. This enabled us to measure the magnetic properties of only the
film and, in addition, to observe signs of the martensitic phase transformation at low temperatures. Due to its high solubility to water, NaCl was a good candidate for the fabrication of free-standing test structures using simple isotropic etching with water. Next we will concentrate on annealing the released films at high temperatures to improve their crystallinity, which is believed to lead to the formation of a stable martensitic phase [13]. The results presented in this article form the basis for studying the effect of iron doping on Ni-Mn-Ga and are the first step towards the fabrication of microscopic FSM components using lithographic techniques.

**Figure 5.** Scanning electron microscope image of one of the Ni-Mn-Ga films deposited on NaCl.

**Figure 6.** Optical microscope image of an air-bridge structure patterned in a Ni-Mn-Ga film.

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