Research Article

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The features of Ni$_2$MnIn polycrystalline Heusler alloy thin films formation by pulsed laser deposition

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Abstract: The Ni-Mn-In-based Heusler alloys belong to the most studied intermetallic compounds due to a variety of physical effects inherent to them, including the shape memory and magnetocaloric effect, field-induced structural phase transition, and others. All of these properties are strongly depend on element concentrations, uniformity, and purity of the structure. Therefore, rather strict requirements are imposed on the synthesis technology of such samples.

We report the dependencies of Ni-Mn-In polycrystalline thin film composition on growth parameters. It was shown that the composition mismatch between sample and target caused by the resputtering of the sample material with high-energy particles of the ablation plume, and the different ablation yields of elements from the target. The main deposition parameters demonstrated (Ar growth pressure, laser energies, substrate temperature and annealing, target-to-sample distance) for the co-deposition process to obtain the Ni-Mn-In Heusler alloy polycrystalline thin films with the martensitic transition.

Keywords: composition transfer, intermetallic films, martensitic transition, co-deposition, laser ablation

1 Introduction

Heusler alloys are a family of more than 1,500 triple intermetallic compounds exceptional properties that are important for various applications. The Ni$_2$MnIn alloy is one of the most studied in this family. It has high values for the magnetocaloric effect [1], shape memory effect, and many others. Most of these effects are based on the martensitic transition and close connection between the magnetic and structural subsystems. The martensitic transition is a structural phase transition from the high-temperature cubic phase (L2$_1$, austenite) to the low-temperature martensitic phase with lower structural symmetry. This transition arises in nonstoichiometric alloy Ni-Mn-In within a narrow interval of concentrations [2].

There are additional applications in the case of thin films [3]. However, when working with nanoscale samples of such compounds—the properties of which significantly depend on external and internal conditions—the parameters of growth procedure become extremely important.

Over the recent years, numerous studies have been dedicated to the synthesis of thin-film samples of Heusler alloy Ni-Mn-In. Thin film samples have been formed using different methods: for example, flash-evaporation [4], thermal co-evaporation [5], molecular beam epitaxy [6], DC magnetron sputtering [7, 8] and pulsed laser deposition (PLD) [9, 10].

Samples should be crystallized during the required structural phase with controlled concentrations of elements. The pulsed laser deposition method completely satisfies the requirements of composition homogeneity and purity.

Previously, we have investigated the dependencies of indium concentrations on the substrate temperature and its influence on magnetic properties in Ni-Mn-In films [11]. Also, the dependencies of structural and morphological properties in MgO/Ni-Mn-In samples were demonstrated [12]. In this paper, we present the results of a complex investigation on the influence of growth parameters on the final composition of thin films. The effects of partial oxidation and resputtering were found, which could explain some previous results. This paper is dedicated to the development of a growth procedure and obtaining thin polycrystalline films of Ni-Mn-In Heusler alloy demonstrating the martensitic transition with the co-deposition procedure.

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2 Experimental details

Two types of pulsed laser (Nd:YAG) deposition experiments were conducted for thin-film sample growth. The first was the deposition of alloyed targets to study the influence of synthesis parameters on concentrations of the elements in the samples. The target Ni$_{50}$Mn$_{34}$In$_{16}$ (Ni-Mn-In alloy with 50% of Ni, 34% of Mn and 16% of In atomic concentrations) composition was synthesized using the arc melting method. Ni, Mn, and In metals with 99.99% purity were used. Ablation has occurred at a laser wavelength of 532 nm, and pulse energy varied from 25 to 325 mJ for different samples with a 0.8 mm$^2$ beam area on the target surface. Substrate temperature varied from 30 to 580$^\circ$C. Deposition took place in a vacuum from $10^{-4}$ to $10^{-8}$ Pa or in Ar buffer gas with the pressures from 0.5 to 7.5 Pa.

The second series of experiments was carried out using the optimal parameters, chosen from the first series. The purpose of these experiments was the synthesis of thin film samples of Heusler nonstoichiometric alloy Ni$_2$MnIn, demonstration of martensitic transition, and study of the dependence of their structural and magnetic properties on element concentrations. Synthesis of the samples was carried out using two simultaneously working Nd:YAG lasers on 532 and 266 nm wavelengths. We used targets of pure metals Ni, Mn and In (99.95%) as well as a combination of alloyed target Ni$_{50}$Mn$_{34}$In$_{16}$ and Mn. Therefore we achieved precise concentration changes from sample to sample. In all cases, we used oxidized (>300 nm oxide thickness) silicon wafer substrates.

Thicknesses and compositions of thin films were investigated using Rutherford backscattering spectrometry (RBS) and energy-dispersive X-ray spectroscopy in the scanning electron microscope (SEM-EDX). Homogeneity of the composition by thickness was determined using the Auger electron spectroscopy (AES) method. Structural properties, including structural phases at different temperatures, were studied using x-ray diffraction (XRD) setup with Cu K-$\alpha$ monochromator beam. Thicknesses about 50nm (from 48 to 54nm) were chosen for all samples.

3 Results and Discussion

3.1 Composition transfer depends on deposition parameters

For a visual demonstration of the influence of deposition parameters on the element concentration in the samples, we will use sputter transfer coefficient $S$ by analogy with [7]. This coefficient expresses the relation of element concentration in the sample to element concentration in the alloy target. Thus, $S_{Ni} = S_{Mn} = S_{In} = 1$ corresponds to a complete stoichiometric transfer.

Figure 1 shows the dependencies of $S$ for all elements on the substrate temperature and pressure of Ar buffer gas for the first series of samples (ablation of target alloy Ni$_{50}$Mn$_{34}$In$_{16}$). Compositions were determined by EDX and RBS.

As shown in Figure 1(a), indium concentration in the sample strongly depends on the substrate temperature. This arises from two mechanisms or their combination: the resputtering of the sample material with high-energy particles of the ablation plume [13], and the different ablation yields of elements from the target [14]. Resputtering might be explained by significant differences between ion sputter yields of compound alloys. For example, sputter yields of the elements are 1.682 for Ni, 2.85 for Mn [15], and 3.2

![Figure 1: The dependency of sputter transfer coefficient $S$ on the substrate temperature (a) and pressure of buffer Ar gas at room temperature (b) during the deposition of samples from Ni$_{50}$Mn$_{34}$In$_{16}$ target](image-url)
for [16] for Ar ions, bombarding normally to the sample plane with energy 1 keV.

To check the different ablation yields effect, SEM-EDX investigations of the alloyed target areas after ablation were made. Areas after >100,000 pulses showed the same element concentrations as pure areas (with no laser damage), which means the selective ablation doesn’t influence on the alloy target.

Thus, there are several ways to deposit Ni-Mn-In Heusler alloy thin films with a required composition:

The first – is the preparation of a new target with a certain composition for each experiment, taking into account the absence of stoichiometric sputter transfer. This approach is the most complicated and expensive since the exact calculation of thin film sample concentrations is quite difficult. The next way is a co-deposition from a few targets. This approach is based on the simultaneous ablation of the manganese or indium targets and the Ni-Mn-In one to obtain the required concentrations. Therefore, this approach allows precisely varying the concentrations in thin film samples using one alloy target. At the same time, the ablation of a pure indium target has a couple of limitations. In its pure state, it is very soft (Mohs hardness is only 1.2) and has a low melting temperature (429K), which leads to many droplets during ablation, whereas, deposition in a noble gas atmosphere might solve this issue [13]. This approach allows decreasing the energy of ions ablated from the target using their inelastic scattering on the noble gas atoms. This process reduces resputtering and increases Mn and In concentrations in the samples.

The last approach is the decrease of laser pulse energy to the ablation edge [13]. The disadvantage is the significant reduction in growth rate, which can lead to an increase of impurities in thin-film samples.

It is possible to combine all listed approaches to eliminate their disadvantages.

To minimize selective ablation and also decrease the kinetic energy of high-energy ablation plume particles, a series of experiments with ablation in low-pressure Ar were conducted. Figure 1(b) shows the dependencies of the sputter transfer coefficient $S$ from target to film samples in noble gas pressure for a series of samples, deposited from the alloyed target $\text{Ni}_{50}\text{Mn}_{34}\text{In}_{16}$. The stoichiometric transfer from the target to the sample could be achieved in low-pressure (~3 Pa) of Ar. However, further increase of the pressure decreased $S$(Mn).

Laser fluence has some influence on stoichiometry transfer too. When pulse energy decreases to the ablation threshold, the sputter transfer coefficient of an element changes (Figure 2).

![Figure 2: The dependence of the sputter transfer coefficient $S$ on laser pulse energy for the series of Ni-Mn-In samples](image)

### 3.2 Manganese oxidation during deposition

The rather high chemical activity of manganese and its ability to oxidate is another feature of the Ni-Mn-In Heusler alloy deposition technology. We found that deposition in a vacuum lower than $10^{-5}$ Pa led to complete oxidation of manganese. Mn oxidation strongly influences the In distribution in thin film depth. Figure 3 shows element distributions by the depth of unannealed Ni-Mn-In samples, deposited in vacuum ~7·$10^{-4}$ Pa, measured by AES with depth ion etching.

In both cases, manganese completely oxidized. At the same time, indium was pushed to the surface and the film-substrate interface to some localization areas.

During the annealing of these samples, the oxidized manganese was extruded from the film to the surface and the interface with the substrate. This resulted in a rather well-defined three-layer film structure (Figure 4a).

To achieve crystallization in the required structural phase, all the deposited at room temperature samples should be annealed. We found that the annealing process required silicon substrates with a thick oxide layer (not less than 300 nm). When using nonoxidized Si substrates, Si deeply penetrated the film.

Therefore, based on what was mentioned above, we can specify some restrictions for Heusler alloy Ni-Mn-In polycrystalline thin film growth by pulsed laser deposition. Firstly, the substrate should be room temperature during the deposition. Next, unoxidized Si substrates are inapplicable due to the diffusion of silicon into the film. To prevent manganese oxidation pressure in the growth chamber should be less than $10^{-6}$ Pa. The pressure of buffer gas (Ar) should be 3-5 Pa in the growth chamber for stoichiometric transfer from target to sample.
Figure 3: The distribution of elements by depth for an as-grown sample of Ni-Mn-In deposited in vacuum $\sim 7 \times 10^{-4}$ Pa, obtained by AES ion profiling.

Figure 4: The distribution of elements by thickness, obtained by AES ion profiling. a) Ni-Mn-In sample, deposited in vacuum $\sim 7 \times 10^{-4}$ Pa at room temperature with the following annealing under $325^\circ$C, b) Ni$_{52}$Mn$_{33}$In$_{15}$ sample, deposited using a two-laser co-deposition Ar atmosphere.

The series of samples with different element concentrations and martensitic transitions were grown using the listed parameters.

3.3 Simultaneous two-laser co-deposition at a low noble gas pressure

As mentioned above, the structural and magnetic properties and martensitic transition in Heusler alloy Ni-Mn-In are strongly dependent on element concentrations. Therefore, one of the goals of this research was to find a way to precisely vary concentrations of the elements in samples. This was achieved using two independent simultaneously working Nd:YAG lasers, operating on 2$^{nd}$ (532 nm), and 4$^{th}$ (266 nm) harmonics. As targets, we used pure metals Ni, Mn, and In with 99.95% purity as well, as a combination of alloyed target Ni$_{50}$Mn$_{34}$In$_{16}$ and Mn. There was a significantly lower droplet density during the manganese ablation compared to indium. Therefore, to obtain the necessary compound of thin-film samples, we adjusted the method of the Ni-Mn-In Heusler alloy thin film deposition, combining the advantages of dual-laser co-deposition and deposition in the low-pressure noble gas. The following conditions were chosen for the deposition:

Substrate: silicon with a thick oxide layer (not less than 300 nm). Substrate being room temperature during deposition. The temperature of annealing was about 350$^\circ$C. Targets: Ni$_{50}$Mn$_{34}$In$_{16}$ alloy, forming by arc-melting in a noble gas atmosphere (remelted a few times for homogeneity), and pure Mn. Argon pressure in the growth chamber: 3 Pa. Laser wavelengths: 532 nm for the
Ni$_{50}$Mn$_{34}$In$_{16}$ target, 266 nm for the Mn target. Pulse repetition rates: 50 Hz for Ni$_{50}$Mn$_{34}$In$_{16}$, 12 Hz for Mn, depending on desired concentration. Pulse energies: 80 mJ for the Ni$_{50}$Mn$_{34}$In$_{16}$ target, 30 to 60 mJ for Mn targets, depending on desired concentration. Annealing temperatures after deposition: 325–350°C, time 1 hour.

High homogeneity (by depth as well as by area) was shown by AES SEM for all samples grown using this technique. Figure 4b shows the distribution of elements by depth, obtained by AES with depth ion etching for the Ni$_{52}$Mn$_{33}$In$_{15}$ sample.

Taking into account a small number of drops, this approach is very useful for obtaining ternary intermetallic compounds.

Using this technique Ni concentration varied from 49 to 52%, Mn from 32 to 34%, and In from 14 to 17%. The series of samples with martensitic transitions were grown. Figure 5 shows XRD patterns of the sample Ni$_{55}$Mn$_{32}$In$_{13}$ with the martensitic transition at different temperatures.

High-temperature L21 austenitic phase transforms to a low-temperature martensitic phase with lower structural symmetry.

4 Conclusions

Based on the investigations of compositions, element distributions, and the morphological, magnetic, and structural properties of Heusler alloy Ni-Mn-In polycrystalline film, the following conclusions can be made. Firstly, the selective resputtering of the elements from the sample surface by high-energy ablation plasma plume particles is the main reason for the nonstoichiometric transfer of the composition from alloy target to sample in high-vacuum experiments. The stoichiometric transfer is possible during ablation in low-pressure (3-5 Pa) Ar. The two-laser co-deposition technique is useful for the synthesis of homogeneous thin films and varying concentrations from sample to sample.

Listed results are very important for deposition technology of intermetallic thin films with the precise composition control by pulsed laser deposition. The features of the martensitic transition in the samples, synthesized by this technique will be published elsewhere.

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