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Pulsed laser deposition of Co-based Tailored-Heusler alloys

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Abstract

Thin films of nonstoichiometric Heusler alloys $Co_2MnSb_xSn_{1-x}$ ($x = 0.2$; 0.4; 0.6; 0.8) have been grown by pulsed laser deposition (double-target/double beam configuration) on Si (1 0 0) substrates using a KrF excimer laser ($\lambda = 248$ nm, $\tau = 20$ ns). The substrate temperature was held at 300 K in all experiments to prevent interface interdiffusion of the species. A comparison between the compositions of films and corresponding targets has been done through energy dispersive X-ray spectroscopy (EDS) analysis showing a very satisfactory match. Scanning electron microscopy (SEM) imaging served to investigate the morphology of the films in order to determine the size and density of droplets which may influence the optical data. Optical conductivity derived from reflectivity measurements shows absorption onsets close to 1 eV, which corresponds to the onset of valence-to-conduction transitions in the minority spin bands theoretically predicted. The values of the saturation magnetisation measured at 300 K on the quaternary alloys are very close to those of ternary ones for which either half-metallic properties or high spin polarisation were theoretically predicted.

Keywords: Quaternary; Alloys; Ternary

1. Introduction

The potential impact in magnetic memory and sensor applications has generated a rapidly expanding interest in integrating magnetoelectronic effects with semiconductor electronics to develop the new area of *spintronics*. In this context, our work addresses the preparation by pulsed laser deposition (PLD) and characterisation of ferromagnetic metal compounds as novel materials in the Heusler system. A spin device requires electrodes that inject a strongly spin-polarised current, and the most promising materials technologies for this are based on high-quality ferromagnetic/semiconductor interfaces. This and the appropriate behaviour of the contacts are most likely the main technological challenges to be overcome before realistic devices can be fabricated. Half-metallic ferromagnets with high Curie temperatures such as Co_2MnX (X = Si, Ge) [1–3] are the right choice for contacts, whereas Co_2MnSn although holding high enough spin polarisation [4], is supposed to be not half-metallic [5]. Hypothetic non-stoichiometric Heusler alloys of the type $Co_2MnZ_{1-x}Z'_x$, such as $Co_2MnSb_{1-x}Sn_x$, are expected to provide a new range of half-metallic materials [5]. *We christen here these quaternary* $Co_2MnZ_{1-x}Z'_x$ *alloys as* ***"tailored-Heusler alloys" (THA)***. Initially called "non-stoichiometric" as referred to the original Heusler structure (Fig. 1a), the Co-based THA are expected to hold tailored physical properties evolving from their hypothetical formula (see for example Fig. 1b).

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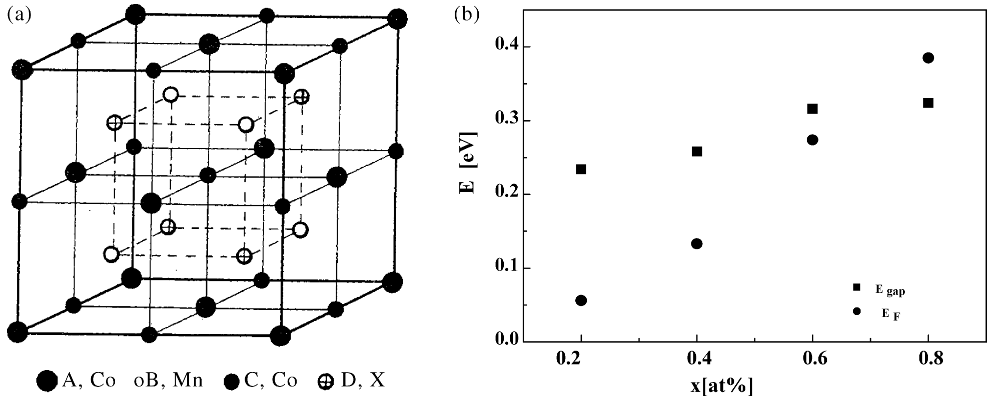

Fig. 1. (a) The Heusler structure. By adjusting the number of electrons of sp elements new half-metallic compounds in the Heusler system can be found. (b) The variation of the gap and of the position of the Fermi level with the composition parameter in THA $Co_2MnSb_xSn_{1-x}$ is linear up to about $x = 0.6$ at% Sb as it results from ref. [5].

Most of the mentioned stoichiometric Heusler alloys have not been fully explored and only very few have been grown on semiconductor substrates, by MBE [6–8] and by sputtering [9]. From the quaternary range $Co_2MnSb_{1-x}Sn_x$ only the alloy with $x = 0.8$ has been partly reported in one of our previous works [10]. Good stoichiometry, morphology and crystalline quality are essential for the films to conserve the ferromagnetic and half-metallic properties of the bulk material. To achieve these requirements we made choice of PLD as a very appropriate technique to produce a stoichiometric transfer from ternary and quaternary bulk to corresponding films [10,11]. This work is devoted to the growth of thin films of $Co_2Mn\ Sb_xSn_{1-x}$ by pulsed laser deposition (PLD) on single crystalline silicon (1 0 0) substrates and investigation of their stoichiometry and optical properties as compared to the targets.

2. Experimental

2.1. Preparation and characterisation of THA PLD targets

The PLD targets of THA $Co_2MnSb_xSn_{1-x}$ ($x = 0.2$; 0.4; 0.6; 0.8) are polycrystalline material seed-less grown by the vertical gradient freeze technique (VGF) from high purity powders (AlfaAesar) of the constituting elements. The detailed growth of the targets is reported elsewhere [11]. The resulting ingots, 22 mm in diameter and 20 mm long after having been rectified, were cut perpendicular to the vertical axis into slices 5 mm thick which were then optically polished and investigated for structure and compositional homogeneity by XRD, SEM and EDS. The Curie temperatures (T_C) of these Co-based THA have been determined from both thermogravimetric analysis (TGA Q500-TA Instruments) and differential scanning calorimetry (DSC 92 SETARAM) at heating/cooling rates of 20 K/min, and compared.

2.2. PLD of THA films and their characterisation

The PLD of these Co-based THA develops with nanosecond pulses of a KrF laser Lambda Physik LPX 220 I ($\lambda = 248$ nm, $\tau = 20$ ns) delivering up to 400 mJ/pulse at frequencies ranging from 2 to 10 Hz and a fluence of 3 J/cm^2 chosen following a study [12] on improving the morphology of the films. The experiments were carried out in high vacuum (10^{-5} Pa). Silicon (1 0 0) substrates hold at 300 K were used in all experiments described here. The cross section of the laser beam is about 2 mm^2, yielding a high enough power density of the laser on the surface of the target to enable nearly congruent ablation of small material amounts if targets of homogeneous composition are used [13]. The films presented here were grown in a double-target/crossed-double beam (2CB) configuration using the set-up in Fig. 2 (IM2-Marseille). Beam incidence at the targets' surfaces happens at angles of 10–45° and the angle between the surfaces of the two targets ranges from 100° to 125°. The propagation axes of the ablation plumes cross at about 10 mm away from the targets. A diaphragm located between the targets and the substrate makes a shield against the direct droplet flux moving more slowly than atoms and ions. The targets-substrate and diaphragm–substrate distances are, respectively, 30–70 and 30–60 mm. The thickness of the films deposited with this configuration was about 110 nm corresponding to 2×10^5 pulses. The growth rate v_{gr} of films was deduced from the thickness of the films as measured by profilometry. SEM imaging was performed with a Philips XL 30 SEM equipped with an EDS microanalysis system. The secondary electron (SE) and the back-scattered electron (BSE) configurations were employed to enable better observation of topography and chemical non-homogeneities. Magnetization was measured versus applied field (H) up to ± 2 T at 50 K intervals from 300 to 10 K, on an Oxford Instruments vibrating sample magnetometer (ICSTM, London). The saturation magnetization in units of Bohr magnetons per formula unit was calculated by assuming a smooth surface and using an uniform film thickness determined by profilometry. The surfaces of the films were perpendicular to the applied magnetic field.

The optical reflectance of both bulk and PLD film samples has been measured over the full UV to IR wavelengths range (0.05–5.0 eV). The resultant dielectric constants of the alloys and their corresponding conductivities have been derived from these measurements using a Kramers Kronig transform.

(a) (b)

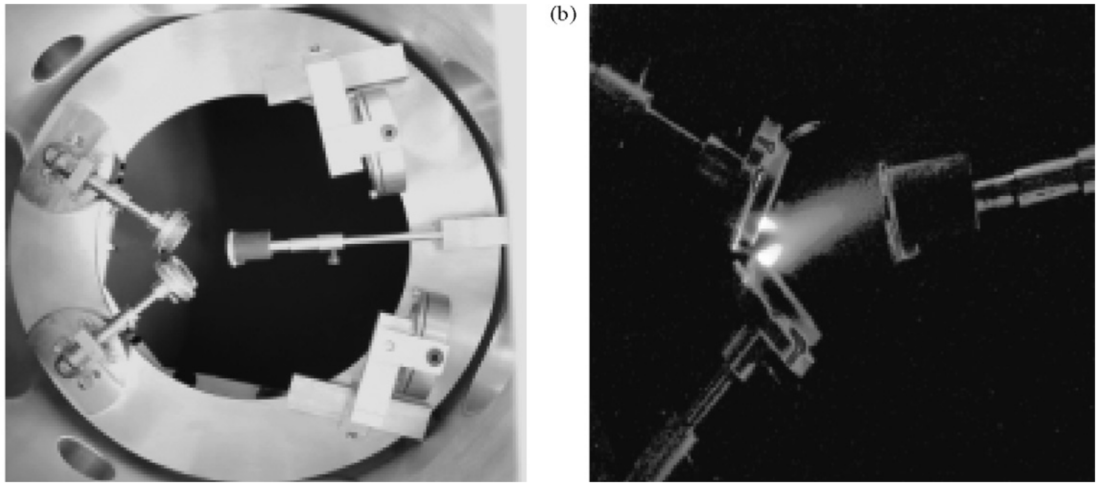

Fig. 2. (a) The double-target PLD set-up at IM2-Marseille. (b) Image taken during double-beam PLD run. The crossed beams through a diaphragm diminish particulates occurrence and reduce their size.

3. Results and discussion

The respective $Co_2MnSb_xSn_{1-x}$ ($x = 0.2$; 0.4; 0.6; 0.8) PLD targets showed homogeneous compositions as it resulted from XRD and EDS analyses.

The compositions of the films and droplets as analysed by EDS and compared with the values for the corresponding targets confirm the stoichiometric transfer by PLD of Co-based THA material from bulk to film (Table 1) already remarked in our previous works on full- and half-Heusler ferromagnetic alloys [10,12,13]. Using the 2CB-PLD configuration with a diaphragm and moderate laser fluences improves the surface morphology of the PLD films as it results from Fig. 3a and b, showing SEM images of two THA films deposited by 2CB-PLD with a diaphragm (a) and without it (b). The density of droplets decreases by two orders of magnitude and their average size reduces from 2 μm to 20 nm, as measured by SEM. Admitting that the layers initiating the growth are even less rough than the termination surface and also the substrate temperature is held as low as 300 K (a new challenge in our PLD experiments with Heusler alloys) enhances, in our opinion, the chance to obtain a ‘‘cleaner’’ film/substrate interface than with other PLD configurations and higher substrate temperatures. However, the deposition rates are much reduced (by a factor of 3) when the 2CB-PLD + diaphragm is employed as compared to 2CB-PLD without a diaphragm.

Table 1
Comparison between the compositions of THA targets' and corresponding PLD films grown by 2CB-PLD

Attempted composition	Composition (normalized to Co) derived from EDS measurements	
	Target	PLD film
$Co_2MnSb_{0.2}Sn_{0.8}$	$Co_2Mn_{0.88}Sb_{0.218}Sn_{0.84}$	$Co_2Mn_{0.9}Sb_{0.21}Sn_{0.79}$
$Co_2MnSb_{0.4}Sn_{0.6}$	$Co_2Mn_{0.895}Sb_{0.4}Sn_{0.62}$	$Co_2Mn_{0.88}Sb_{0.42}Sn_{0.6}$
$Co_2MnSb_{0.6}Sn_{0.4}$	$Co_2Mn_{0.925}Sb_{0.624}Sn_{0.436}$	$Co_2Mn_{0.9}Sb_{0.614}Sn_{0.418}$
$Co_2MnSb_{0.8}\ Sn_{0.2}$	$Co_2Mn_{0.965}Sb_{0.84}Sn_{0.23}$	$Co_2Mn_{0.9}Sb_{0.85}Sn_{0.195}$

The variation of the lattice parameter with composition in the targets as calculated from XRD patterns is shown in Fig. 4a and the evolution of T_C with the compositional parameter x is depicted in Fig. 4b. The lattice constant of the Co-based THA

(a) (b)

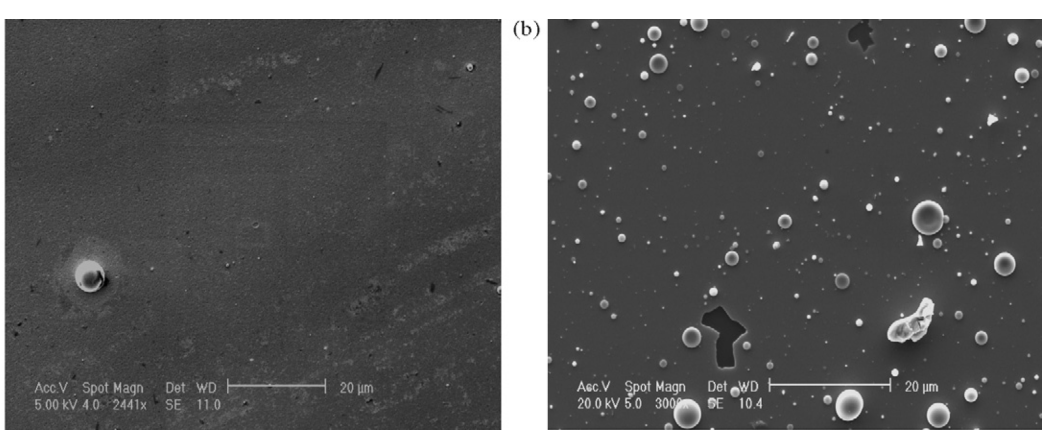

Fig. 3. THA film deposited by 2CB-PLD: (a) with a diaphragm; (b) without a diaphragm. It is to remark that the density and size of the droplets are drastically reduced when a diaphragm is employed.

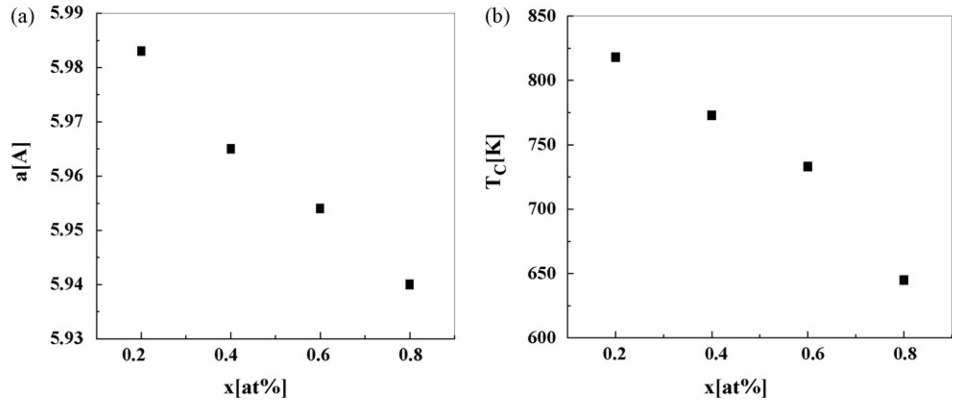

Fig. 4. The variation of the lattice parameter (a) and of the Curie temperature (b) with composition in the THA $Co_2MnSb_xSn_{1-x}$ grown by VGF for PLD targets.

investigated here and their Curie temperature both show linear variations with $-x$ (the composition parameter) over the range 0.2–0.8 at% as it results from Fig. 4, whereas the width of the gap in the minority spin band and the position of the Fermi level in the gap vary linearly with x up to around $x = 0.6$ at% (Fig. 1 built on data derived from ref. [5]). This makes one think that THA properties depending on structure can be tailored according to the above observations. The technical limits of the TGA equipment (amount of material necessary for one measurement) did not allow for measuring T_C of the PLD films. However, close values are expected baring in mind the good reproducibility of the THA composition of the PLD targets in the corresponding films as well as the magnetisation measurements (Fig. 5) performed on the PLD samples. One should still account for ordering effects in the films arising from lattice-mismatched substrates. Ideally, the substrates should be chosen according to the tailored lattice parameter of the THA to be grown. The real part of the conductivity for two Co-based THA PLD films and for a stoichiometric Heusler known to exhibit half-metallic properties (Co_2MnSi) is displayed in Fig. 5 for comparison. It is to remark that both the Heusler and the THAs show similar structures in the higher energy range around 1 eV and above. This is in agreement with previously published

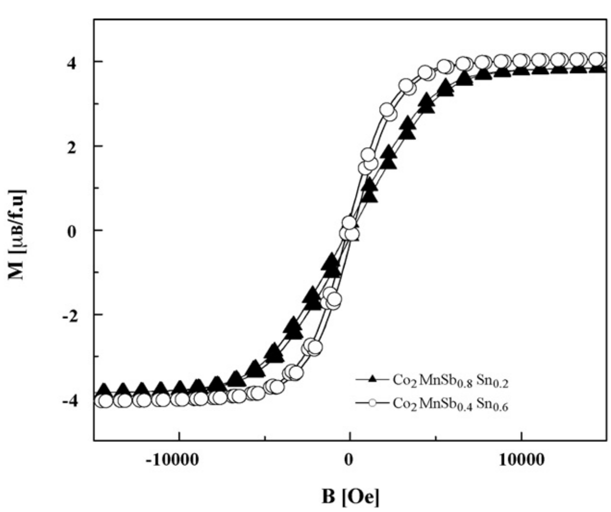

Fig. 5. Room temperature magnetisation loops of $Co_2MnSb_xSn_{1-x}$ ($x = 0.2$ and 0.4) PLD films.

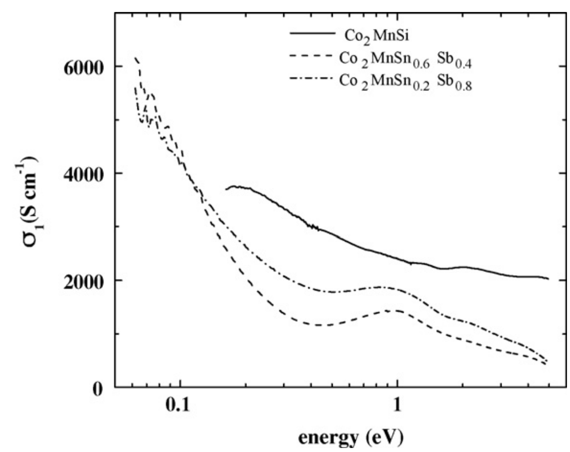

Fig. 6. Optical conductivity of two THA samples in the series $Co_2MnSn_{1-x}Sb_x$ as compared to the one measured on Co_2MnSi prepared with the same technique. Band structure calculations for this latter one predict 100% spin polarization at the Fermi level.

theoretical band structure calculations [8,14] although the structures appear broadened and attenuated. However, in the infrared, where free electron signatures, indicative of half metallicity, are predicted for all these systems, substantial differences are apparent. Stoichiometric alloys such as Co_2MnSi exhibit distinctly semiconducting behaviour as indicated by a lower than unity conductivity in the low frequency range although showing some oscillator strength in the energy region below 1 eV. For the THA $Co_2MnSb_xSn_{1-x}$ samples, with x covering the full range, the reflectance and calculated real conductivity indicate definite metallic behaviour with a Drude-like edge located around 0.2 eV for all samples (Fig. 6). Although a pure Drude expression does not account well for the edge, the difference in this edge between the various alloys is likely indicative of different electron scattering lifetimes with x.

4. Conclusions

We have prepared ferromagnetic Co-based Tailored Heusler Alloys in bulk and PLD films starting from their hypothetical formula advanced by Ishida et al. [5]. A satisfactory match between the composition of the bulk THA targets and the corresponding PLD films confirms PLD as a good choice for a technique to produce thin films of these quaternary alloys. The 2CB-PLD process using a diaphragm improves the surface morphology of the THA films and reduces the growth rate by a factor of 3 in comparison with the runs carried out with double target/double beam in the absence of the diaphragm. A linear decrease of the lattice parameter and of the Curie temperature is experimentally observed with increasing compositional parameter x for Sb. The room temperature magnetization of the Co-based THA PLD films we have prepared exhibit saturation values comparable with those reported for stoichiometric Heusler alloys predicted to be half metals. From optical conductivity measurements it looks like the variation in the value of x having less effect on carrier numbers (and hence band structure at the Fermi level) than on actual scattering of the carriers. In summary, we may tentatively ascribe the different behaviour of ternary and quaternary (THA) Heusler alloys to different susceptibility to disorder at the atomic level. The above results would indicate that quaternary alloys show less susceptibility to disorder than the ternary alloys.

Acknowledgments

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