Pulsed Laser Deposition of Cd$_{1-x}$Mn$_x$Te Thin Films

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I. INTRODUCTION

The semimagnetic semiconductor Cd$_{1-x}$Mn$_x$Te is a very interesting material due to its various properties connected with the presence of the Mn ion (an almost linearly increase of energy gap when the Mn concentration increases [1], a change of lattice constants by varying the Mn content, a giant Faraday rotation near the fundamental absorption edge, for which the spin-exchange interaction between the 3d electrons of the Mn$^{2+}$ ions and the conduction band electrons is responsible [2]). This last property is of interest in the design of all-optical magnetic field sensors. All-optical sensors are of great interest to be used in high intensity electric and radiation fields.

Pulsed laser ablation deposition (PLD) is emerging as a well-suited technique for the deposition of thin films of complex materials like Cd$_{1-x}$Mn$_x$Te since, unlike the evaporation processes, it preserves the stoichiometry of the target.

The aim of this work is the deposition by PLD of Cd$_{1-x}$Mn$_x$Te thin films with various Mn concentrations by XeCl excimer laser and the study of their optical, morphological and compositional characteristics. Due to the peculiarities of the composition of this material, PLD could be a successfully technique in producing thin films of this material.

II. EXPERIMENTAL APPARATUS

Depositions by PLD were performed in a stainless-steel chamber under high vacuum ($10^{-5}$ Pa). A XeCl excimer laser ($\lambda=308$ nm, $\tau=30$ ns) was used. Cd$_{1-x}$Mn$_x$Te targets with different values of Mn concentration ($x=0.05$, 0.36 and 0.43) were used. Each deposition was accomplished with 40000 laser pulses at the repetition rate of 10 Hz. Before starting each deposition, the irradiated target area was cleaned with 1000 successive laser pulses to remove oxide and pollution, with the substrate protected by a mask. The laser fluence was set at 6 J/cm$^2$. During irradiations, the targets were rotated at 3 Hz to avoid fast drilling of the disks. The films were deposited on sapphire (Al$_2$O$_3$) and on <100> Si substrates placed at 40 mm from the target. The substrate holder was resistively heated at a temperature of 250 °C, to promote crystallization of the films during the deposition process. After deposition, the substrate was slowly cooled to room temperature to avoid thermal stresses.

Various diagnostic techniques were used for the characterization of the deposited films. SEM was used to study the surface morphology. EDS was used to study the composition of the deposited films in comparison with the respective targets. Computer simulations of RBS spectra, recorded with 2.2 MeV He$^+$ ions, allowed determining the film thickness [3]. The structure of the films was studied with XRD in the Bragg-Brentano configuration with a CuK$_\alpha$ source. Optical transmission spectrometry (OTS) in the 200-3500 nm range was used to determine the absorption edge and the energy band-gap of the films.

III. RESULTS AND DISCUSSION

SEM inspections showed that the films deposited from targets with low Mn concentration ($x=0.05$) present a plain surface, without corrugations, cracks or voids, only sub-micron droplets were detected. The density and dimensions of the droplets increase dramatically with increasing $x$ values, this is probably due to the deficiency of Cd in the films. A shorter laser wavelength could help to improve the film morphology, as it happened in our work on deposition of silica thin film [4].

From computer simulation of RBS spectra it results that the thickness of the films, deposited with 40000 laser pulses, is in the range 0.5-0.6 µm (Table 1).

<table>
<thead>
<tr>
<th>T</th>
<th>d (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd$<em>{0.95}$Mn$</em>{0.05}$Te</td>
<td>600</td>
</tr>
<tr>
<td>Cd$<em>{0.64}$Mn$</em>{0.36}$Te</td>
<td>530</td>
</tr>
<tr>
<td>Cd$<em>{0.57}$Mn$</em>{0.43}$Te</td>
<td>600</td>
</tr>
</tbody>
</table>

Table 1: film thickness, as inferred from computer simulations of the experimental RBS spectra.

T: target composition; d: film thickness (40000 laser pulses).

From the RBS spectra it is not possible to correctly determine the concentration in the films of the three atomic components Cd, Mn and Te.

From the analysis of EDS spectra, it is evident that the Cd concentration is more or less halved in the films deposited from targets with $x=0.36$ and 0.43, with respect to the film deposited from the target with $x=0.05$.

A more quantitative, although indirect, approach to the stoichiometry of the films can be obtained from the analysis of the optical transmission spectra recorded in the range 200 – 3500 nm (Fig.1).
From the transmission data it is possible to calculate the band-gap energy and consequently the percentage of the Mn in the deposited films [5]. The energy gap at room temperature is given by the relation $E_{gth}=1.528+1.316x$ eV [1].

![Optical transmission spectra of the films deposited from the target Cd$_{0.95}$Mn$_{0.05}$Te (---), Cd$_{0.64}$Mn$_{0.36}$Te (····) and Cd$_{0.57}$Mn$_{0.43}$Te (---).](image)

**FIG. 1: Optical transmission spectra of the films deposited from the target Cd$_{0.95}$Mn$_{0.05}$Te (---), Cd$_{0.64}$Mn$_{0.36}$Te (····) and Cd$_{0.57}$Mn$_{0.43}$Te (---).**

Stoichiometric films should present the energy gap (EG) values listed in Table 2 as $E_{gth}$. From OTS it is possible to determine the EG values of the films (listed in Table 2 as $E_{exp}$). The results show that film stoichiometry is not so far from the one of the relative target, although the films present a lower Cd concentration, as expected. Cd deficiency is due to the substrate heating, which lowers the sticking coefficient of the element and increases its evaporation rate (the melting point of Cd is ~321 °C). In fact, samples deposited on substrates at room temperature show the same composition of the target [6]. The problem of Cd deficiency in films deposited on heated substrate can be overcome by increasing the rate of Cd atoms impinging on the growing film by supplementary Cd evaporation [7], or by ablating targets richer in Cd.

<table>
<thead>
<tr>
<th>Target</th>
<th>$E_{gth}$ (eV)</th>
<th>$E_{exp}$ (eV)</th>
<th>Film</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd$<em>{0.95}$Mn$</em>{0.05}$Te</td>
<td>1.59</td>
<td>1.65</td>
<td>Cd$<em>{0.91}$Mn$</em>{0.09}$Te</td>
</tr>
<tr>
<td>Cd$<em>{0.64}$Mn$</em>{0.36}$Te</td>
<td>2.00</td>
<td>2.15</td>
<td>Cd$<em>{0.33}$Mn$</em>{0.47}$Te</td>
</tr>
<tr>
<td>Cd$<em>{0.57}$Mn$</em>{0.43}$Te</td>
<td>2.09</td>
<td>2.26</td>
<td>Cd$<em>{0.43}$Mn$</em>{0.56}$Te</td>
</tr>
</tbody>
</table>

Table 2: target and the theoretical energy gap $E_{gth}$ obtained from the relation $E_{gth}=1.528+1.316x$ eV, compared to the experimental energy gap $E_{exp}$ and the deduced film composition.

From the OTS we can infer an optical cut off at $\lambda=750$ nm (corresponding to $E_{exp}=2.15$ eV) and $\lambda=547$ nm (corresponding to $E_{exp}=2.26$ eV) for the films obtained by ablating targets with $x=0.05, x=0.36$ and $x=0.43$, respectively. As seen in Table 2, the experimental values of $E_{exp}$ are always higher than the expected one in the films with the same composition as the target. The difference $E_{exp}-E_{gth}$ increases with increasing $x$. This fact is due to the deficiency of Cd in the films with respect to targets, and corroborates the same conclusions inferred from SEM inspsection.

The XRD spectra were recorded from the samples deposited on $<100>$ Si substrates, since the sapphire substrate precludes a correct discrimination of the peaks. Spectra show a polycrystalline structure of the deposited films. Besides peaks from the Si substrate, the cubic CdTe phase and the MnTe$_2$ phase can be detected.

IV. CONCLUSIONS

Cd$_{1-x}$Mn$_x$Te films (0.5–0.6 µm) were deposited on sapphire and $<100>$ Si substrates heated at 250 °C by XeCl laser ablation of targets with different Mn content ($x=0.05, 0.36$ and $0.43$). The film resulted polycrystalline with a composition in quite good agreement with the one of their relative targets, but a Cd deficiency was observed in all the deposited films. The surface morphology is good for films with low Mn concentration ($x=0.05$), but it deteriorates with increasing Mn concentration for the appearance of droplets. From transmission spectroscopy the absorption edges and the band-gap energies were determined. From these data the effective Mn concentration in the films was calculated. We conclude that the PLD process with excimer lasers is well suited to deposit polycrystalline Cd$_{1-x}$Mn$_x$Te films at relatively low temperature. It must be taken into account that heating of the substrate causes a deficiency of Cd in the films, which in turn affects the surface morphology of the films. When strict preservation of the target composition is needed and heating of the substrate is mandatory to get well-crystallized films, ablations should be accomplished in a low pressure Cd atmosphere.