The influence of substrate temperature and annealing on the properties of pulsed laser-deposited YIG films on fused quartz substrate

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A B S T R A C T

Yttrium iron garnet (YIG) thin films were deposited on fused quartz substrate at different substrate temperatures (T_s) varying from room temperature (RT) to 850 °C using pulsed laser deposition (PLD) technique. All the films in the as-deposited state were X-ray amorphous and non-magnetic at RT. The film deposited at RT after annealing at temperatures T_a ≥ 700 °C showed both X-ray peaks and the magnetic order. The films deposited at higher T_s (500–850 °C) and then annealed at 700 °C resulted in better-quality films with higher 4πM_s value. The highest value of magnetization was for the sample deposited at 850 °C and annealed at 700 °C, which is 68% of the bulk 4πM_s value.

Keywords:
YIG
PLD
Thin film
Magnetization
XRD

1. Introduction

Ferrite thin films are considered as potential candidates for magnetic and magneto-optical recording media applications, and hence are being studied since several years [1–4]. These films require a thermal treatment either in the form of substrate heating while deposition or in the form of post-deposition annealing to optimize their properties. Even after thermal treatment the magnetic properties of the films have been reported to be different from their bulk counterparts [5–9]. Recently, there has been interest in the deposition of thin films of yttrium iron garnet (YIG) [7,9–11]. Unlike the spinel ferrites, the magnetization in these films, when deposited on fused quartz substrates using pulsed laser deposition (PLD), can even become larger than the bulk values [7]. It has, however, been shown by us that the properties of PLD YIG thin films are very much dependent on the nature of the substrate [9,11]. Single phase, YIG thin films with saturation magnetization (4πM_s) value close to that of the bulk have been grown on single-crystal Gd3Ga5O12 (GGG) substrates [9]. YIG thin films when deposited on Si substrate, on the other hand, have resulted in nanocrystalline YIG mixed with orthoferrite (YFeO3) phase, with lower 4πM_s value [11].

In the present paper, we present a study on the influence of thermal treatment on the evolution of structural and magnetic properties of YIG thin films deposited by PLD on fused quartz substrates.

2. Experimental details

The PLD has been employed to deposit polycrystalline YIG thin films on fused quartz substrates using a stoichiometric YIG target. The third harmonic (355 nm) of Nd:YAG (yttrium aluminum garnet) laser, with 10 Hz repetition rate and 5–6 ns pulse width, was used to ablate the target. Typical fluence of the laser beam on the target, kept at a distance of 4.5 cm from the substrate, was 2.5 J/cm². The depositions were carried out in pure oxygen pressure of 0.16 mbar at different substrate temperatures (T_s) varying from room temperature (RT) to 850 °C. Here, the RT means a deposition at the ambient substrate temperature in the chamber without heating or cooling the substrate. Some of the films were subjected to a post-deposition annealing (ex situ) in air for 2 h.
The thicknesses of the films were measured by stylus profilometer and were around 200 nm. X-ray diffraction (XRD) $\theta$–$2\theta$ scans were made to investigate the structural properties of the thin films. Magnetic measurements were carried out at ambient temperature (298 K) using a vibrating sample magnetometer (VSM). The magnetic hysteresis ($M$–$H$) loops of all the samples were recorded in parallel configuration (in-plane), i.e. with the field applied along the film plane. The $M$–$H$ loops were corrected for diamagnetic substrate contribution. The optical microscopy and the scanning electron microscope were used to examine the surface quality of these films. It was observed that films were almost free from any crack. Also, the films showed a very good adherence to the substrate, as even the ultrasonic treatment in organic solvents such as acetone and isopropyl alcohol did not peel the films off.

3. Results and discussion

The XRD of YIG thin films deposited at different $T_s$ is shown in Fig. 1. It is seen that the films deposited in the entire $T_s$ range (RT to 850 °C) do not show any sharp peak. The absence of sharp peaks in the as-deposited ferrite films without any substrate heating is quite common, and is related to the nanocrystalline nature of the sample. These films when examined by transmission electron microscopy (TEM) normally show clear rings with a very small grain size [12,13]. To increase the grain size to a level where XRD peaks could be observed, the films have to be subjected to a thermal treatment. This treatment can either be in the form of a substrate heating or a post-deposition annealing or a combination of both. As an example, Bohra et al. [5] observed no sharp XRD peak in the case of PLD Zn ferrite thin films on quartz substrates when deposited at RT, but peaks were observed for $T_s \geq 200$ °C. Similarly, Popova et al. [7] observed, in the case of PLD YIG thin films on quartz substrate, that films were devoid of any sharp XRD peaks when prepared at low $T_s$ ($\leq 400$ °C), but the same could be observed for $T_s$ above 400 °C. They deposited YIG thin films with relatively higher laser fluence (3–9 J/cm$^2$) and in lower oxygen pressure (0.04 mbar). Dumont et al. [14] have deposited oxygen off-stoichiometric YIG thin films on SiO$_2$ substrates using PLD by varying the base oxygen partial pressure between 15 and 400 mTorr. They observed that the polycrystalline single-phase YIG, with slight texture could be grown at 840 °C of substrate temperature and 30 mTorr of oxygen pressure. Sui and Kryder [15] and Dash [16], on the other hand, reported that sputter-deposited M-type barium ferrite thin films on Si substrates, and lithium zinc ferrite thin films on quartz substrate deposited at ambient substrate temperature start showing sharp XRD peaks after post-deposition annealing at or above 700 and 750 °C, respectively. In our earlier study of PLD YIG thin films on single-crystal Si(10 0) and GGG(111) substrates, XRD peaks were seen when films were deposited at $T_s \geq 600$ and 750 °C, respectively [9]. It is, therefore, quite interesting that in our present case we do not see any XRD peak even when films are deposited at $T_s$ of 850 °C. These results clearly demonstrate that both the deposition conditions and the nature of the substrate play a vital role in the grain growth in the YIG films deposited by PLD. Moreover, just the substrate heating during deposition is not enough for the grain growth when amorphous quartz substrates are used.

In order to see if post-deposition annealing will help in the observation of XRD peaks, we annealed the RT-deposited film at temperatures ($T_a$) varying between 600 and 800 °C. Fig. 2(a) shows XRD of such annealed films for different $T_a$. As is clear from this figure, XRD peaks, indexed to single-phase YIG (standard JCPDS file no. 43-0507), were seen for $T_a \geq 700$ °C. It is noteworthy that the film annealed at the highest $T_a$ of 850 °C, shows two peaks other than YIG. These additional peaks can be indexed to (10 0) and (10 1) of SiO$_2$. The presence of additional peaks can be because of reasons like crystallization of quartz substrate along with probable diffusion between the film and the substrate.
The above results indicate that post-deposition annealing of PLD YIG thin films deposited on fused quartz substrates even at a lower temperature is more beneficial in the grain growth than the substrate heating. However, we do not observe such a post-deposition annealing effect on PLD YIG thin films when deposited on Si and GGG substrate. We carried out a second experiment in which the films deposited at higher \( T_s \) (500–850 °C), were also annealed at 700 °C. Fig. 2(b) shows the XRD of the films deposited at different \( T_s \) and annealed at 700 °C. The XRD of the YIG target has been given for the comparison in the same figure. As we can see from this figure that all the films now show many sharp XRD peaks, which can be indexed to YIG phase. It has also been observed that the positions of these peaks are close to the bulk, while the relative intensities of different \((hkl)\) planes differ from the bulk, as well as standard JCPDS data.

Table 1 shows the relative intensities of different \((hkl)\) planes of YIG thin films deposited at various temperatures and annealed at 700 °C. The JCPDS and the target values are also given for comparison. It is seen from this table that only for the sample deposited at 750 °C all the peaks are seen. For other samples we see a smaller number, the least being three for the sample deposited at RT. More importantly, the intensities of the peaks that are seen are not always similar to those seen in bulk. As an example, though for RT-deposited sample, the relative intensities of all the observed peaks are close to that of bulk but \((640)\) and \((642)\) peaks are not seen. This is in spite of the fact that the intensities of these peaks in bulk are quite high and similar to the observed \((420)\) and \((422)\) peaks. Similarly, in 750 °C sample \((321)\) peak is seen with much larger intensity than the bulk. We feel that this phenomenon is because the films are textured due to non-random distribution of grains. What is interesting from this table is that this texture seems to also depend on the temperature at which the film is deposited. The value of lattice constant calculated for these films, were found to be between 12.346 and 12.360 Å (smaller than the bulk value ‘12.376 Å’) and do not show any systematic change with the substrate temperature.

We measured the magnetization of all the films. No \( M-H \) loop was observed for the as deposited films irrespective of the \( T_s \), indicating that the nanocrystalline state of these films prevented the magnetic order at RT which is a well-known phenomenon. The \( M-H \) loops started appearing only after annealing the films at 700 °C, in accordance with the observation of the sharp XRD peaks. Fig. 3 shows the \( M-H \) loop for YIG thin film deposited at 850 °C and annealed at 700 °C. The maximum applied field was 5 kOe, however, for clarity the loop up to a field of 2 kOe has been amplified and shown in the figure. The loop up to a field of 5 kOe has only been shown in the inset. Similar \( M-H \) loops were observed also for the film deposited at RT and annealed at 700 °C.

<table>
<thead>
<tr>
<th>((hkl))</th>
<th>JCPDS</th>
<th>Bulk</th>
<th>( T_s )</th>
<th>RT</th>
<th>500 °C</th>
<th>750 °C</th>
<th>800 °C</th>
<th>850 °C</th>
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<tbody>
<tr>
<td>(321)</td>
<td>3</td>
<td>3</td>
<td>–</td>
<td>39</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>(400)</td>
<td>30</td>
<td>33</td>
<td>46</td>
<td>36</td>
<td>24</td>
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<td>(420)</td>
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<tr>
<td>(422)</td>
<td>44</td>
<td>46</td>
<td>30</td>
<td>40</td>
<td>39</td>
<td>29</td>
<td>32</td>
<td></td>
</tr>
<tr>
<td>(640)</td>
<td>40</td>
<td>34</td>
<td>–</td>
<td>29</td>
<td>18</td>
<td>14</td>
<td>&lt;10</td>
<td>&lt;10</td>
</tr>
<tr>
<td>(642)</td>
<td>47</td>
<td>36</td>
<td>–</td>
<td>25</td>
<td>24</td>
<td>&lt;10</td>
<td>&lt;10</td>
<td></td>
</tr>
</tbody>
</table>

The relative intensities of bulk YIG target and Standard JCPDS file has given for the comparison.

Table 2

<table>
<thead>
<tr>
<th>( T_s ) (°C)</th>
<th>600</th>
<th>700</th>
<th>800</th>
<th>1000</th>
<th>300</th>
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<tbody>
<tr>
<td>( 4\pi M_s ) (G)</td>
<td>No loop</td>
<td>800</td>
<td>900</td>
<td>1100</td>
<td>950</td>
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</table>

Table 3

<table>
<thead>
<tr>
<th>( T_s ) (°C)</th>
<th>RT</th>
<th>500</th>
<th>750</th>
<th>800</th>
<th>850</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 4\pi M_s ) (G)</td>
<td>800</td>
<td>900</td>
<td>1100</td>
<td>950</td>
<td>1150</td>
</tr>
</tbody>
</table>

\( T_s > 700 \) °C and also for the films deposited at different \( T_s \) (500–800 °C) and annealed at 700 °C. The \( M-H \) loops, however, do not saturate even at 5 kOe. This phenomenon is attributed to the high-field susceptibility (HFS) as reported in the literature [5,9,17]. The \( 4\pi M_s \) values were then obtained by drawing tangential line from the high-field loops to the zero field. The intercepts on y-axis were taken as the \( 4\pi M_s \) values, which represent spontaneous magnetization of the samples. These values are listed in Table 2 for the RT-deposited YIG thin films and annealed at different temperatures. It is surprising to note here, that the film deposited at the highest \( T_s \) of 850 °C does not show any magnetization in the as-deposited state, but the sample deposited even at RT and annealed at a relatively lower temperature of 700 °C shows magnetic order. The value of \( 4\pi M_s \) is observed to be 800 G for the film deposited at RT and annealed at 700 °C and it increases to a value of 1000 G when the film is annealed at 800 °C. The \( 4\pi M_s \) of the film annealed at 850 °C is found to decrease drastically to 300 G and may be because of the damaging of the film as discussed earlier in the XRD results.

Table 3 shows the \( 4\pi M_s \) values for the films deposited at different temperatures but all annealed at 700 °C. It is seen that the \( 4\pi M_s \) value generally increases with \( T_s \) irrespective of the annealing temperature, which has been kept constant at 700 °C. Moreover, the maximum value of magnetization (1150 G) has been observed for the film deposited at 850 °C and also annealed at 700 °C. The coercivity (\( H_c \)) value in these films on the other hand was found to be between 55 and 90 Oe. The grain size of PLD-YIG thin films deposited at different \( T_s \) and annealed at 700 °C, were estimated using Scherrer’s formula and also by atomic force...
microscope (AFM) image and found to be between 70 and 145 nm. No systematic change in $H_c$ value with the grain size in these films was observed.

It is also to be remarked that magnetization values in our PLD YIG thin films on quartz substrates are always lower than the bulk value (1750 G). The $4\pi M_s$ value close to the bulk (≈96% of the bulk) had been reported when PLD YIG thin films were deposited on single-crystal GGG substrate, while a very small value of $4\pi M_s$ (maximum of 28% of the bulk) had been observed when YIG thin films were deposited on Si substrates [9,11]. The lowering in $4\pi M_s$ in the later case was explained due to the presence of orthoferrite phase with nanocrystalline grains. The lower value of magnetization as compared to the bulk in ferrite thin films have been commonly observed both in the case of PLD and the sputtered films by several workers [5,17]. It is generally believed that when the grain sizes are small a significant ratio of the material lies in the grain boundary. This grain boundary material is neither properly crystallized nor properly ordered magnetically, and thus is responsible for reduced magnetization. As the grain sizes grow upon annealing, the grain boundary material decreases causing an increase in the magnetization [7,9].

Another interesting result from this study is that two different methods of thermal treatment viz., the substrate heating and the ex-situ annealing cause different effects in the film properties. While 850 °C annealing leads to a deterioration of the film, the same thing does not happen when the films are actually deposited at the same substrate temperature. This shows that these two phenomena are basically different.

4. Conclusions

In this paper, we present the study of the PLD YIG thin films deposited at various substrate temperatures up to 850 °C. We find that the as-deposited films neither show any XRD peak nor any magnetic order. However, annealing even at a temperature of 700 °C, helps in the development of the magnetic order. Thus annealing plays a more important role in improving the properties of the films in comparison of the high-temperature deposition. Moreover, a film deposited at higher substrate temperature shows higher magnetization than the RT-deposited film, even when both are subjected to the same annealing temperature. Thus it requires both high-temperature deposition and the post-annealing to deposit good YIG films by PLD on quartz. The highest value of magnetization that has been observed by us is for the sample deposited at 850 °C and annealed at 700 °C. However, this value is only 68% of the bulk $4\pi M_s$ value. Thus, the values of magnetization of YIG samples on quartz substrates are smaller than those deposited on GGG substrate.

References