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Investigation of induced parallel magnetic anisotropy at low deposition temperature in Ba-hexaferrites thin films

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ABSTRACT

In this paper we present the effect of low substrate temperature on structural, morphological, magnetic and optical properties of Ba-hexaferrite thin films. Films were deposited on single crystal Silicon (1 0 0) substrate employing the Pulsed Laser Deposition (PLD) technique. The structural, morphological, magnetic and optical properties are found to be strongly dependent on substrate temperature. The low substrate temperatures (room temperature to 200 °C) restrict the formation of larger grains. For the higher substrate temperature i.e., 400 °C, the grain size of the deposited thin film are much larger. The film grown at low substrate temperature do not show any anisotropy. As the substrate temperature is increased, the easy axis of the films alinged itself in the direction parallel to the film plane whereas the hard axis remained in the perpendicular direction. The higher substrate temperature caused the uniaxial magnetic anisotropy, which is very important in magnetic recording devices. The saturation magnetization and optical band gap energy values of 62 emu/cc and 1.75 eV, respectively, were achieved for the film of thickness 500 nm deposited at 400 °C. Higher values of coercivity, squareness and films thickness are associated with the growth of larger grains at higher substrate temperature.

1. Introduction

Hexagonal ferrites are important magnetic oxides in thin film technology due to their high resistivity, high uniaxial magnetic anisotropy field and moderate saturation magnetization values [1]. Unlike magnetic metals, ferrites are transparent to RF and microwave frequencies, therefore they have the potential of being used in monolithic microwave integrated circuitry (MMIC), in magnetic recording devices and for high frequency applications [2,3].

The hexagonal unit cell of barium ferrite contains two formula units, or $2\times32=64$ total atoms [4]. It is very long in c direction, with $c=2.32$ nm and $a=0.588$ nm. The barium and oxygen ions are both large and nonmagnetic see in Fig. 1 [5]. They are arranged in closely packed fashion. The relatively smaller Fe^{3+} ions are located in the interstices. The only magnetic ions in the barium ferrite are Fe^{3+}, each with the moment of 5 μ_B. The Fe^{3+} cations in the hexagonal unit cell are arranged in three crystallographically different sites: one tetrahedral, three octahedral and one pseudo-tetrahedral sublattices. By the known spin directions of the Fe^{3+} ions in the cubic section of the cell and by applying the superexchange interaction principle, one can predict the direction of its spin moment. In this way one arrives at the predicted value, per cell, of 16 ions with spin in one direction and 8 ions with spins in opposite direction. The predicted magnetic moment per cell is therefore $(16-8)\times(5)=40$ μ_B or 20 μ_B per molecule of $BaO.6Fe_2O_3$. This quantity corresponds to $M_s=380$ emu/cc at 20 °C [6].

Several techniques such as liquid phase epitaxy, RF magnetron sputtering, solgel and PLD [7–11] have been employed to deposit BaM thin films. Most of these studies have used c-plane sapphire (Al_2O_3) as substrates for achieving a good orientation. However, because of large lattice mismatch between BaM and Sapphire (substrate), the thin BaM films (up to 100 nm) are highly strained. This strain causes a significant degradation in the structural as well as in the magnetic properties of films [12]. Moreover, the high cost of sapphire has hindered its application in industry.

Recently, hexaferrite thin films fabricated by the pulsed laser deposition technique on Si received much more attention [13,14].

PLD is a versatile and fast method for the deposition of high quality thin films and appears to be more effective in fabricating thin films of oxide materials (compounds) than other techniques [15]. The main advantage of this technique is to preserve the

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stoichiometry of the target material on the film after deposition. In our previous work single crystal *c*-axis Ba-hexaferrites thin films on sapphire substrate was deposited using Nd. YAG laser [16].

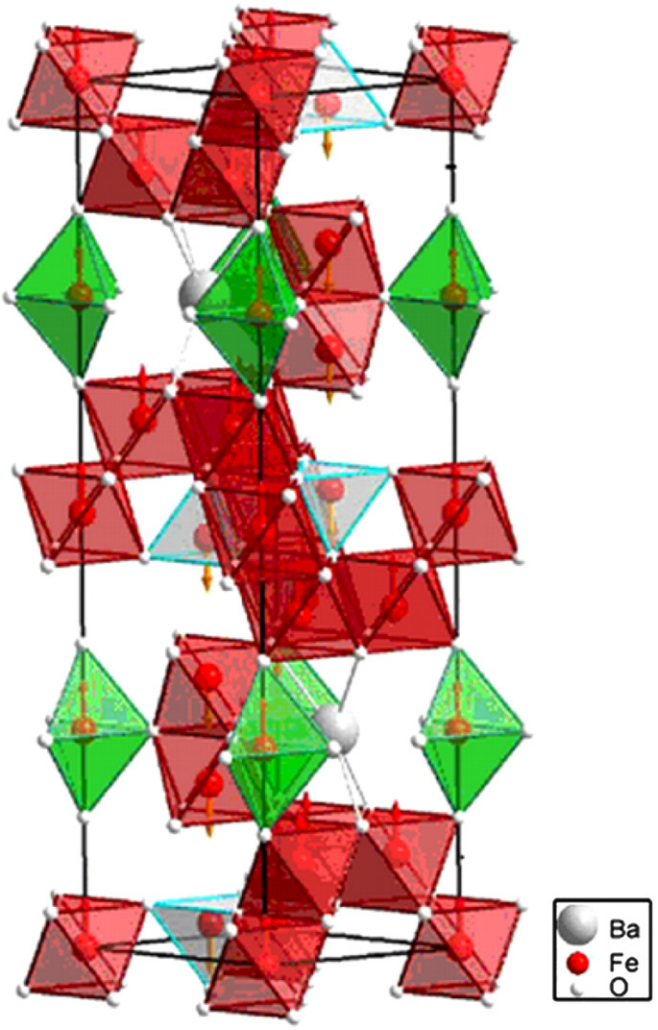

Fig. 1. Schematic diagram of Barium hexaferrite M-type structure [5].

A long sought goal of the ferrite community has been the integration of ferrite-based microwave passive devices with semiconductor electronics. This requires the growth of ferrites on semiconductor substrates. Oriented hexaferrite films to be deposited on semiconductor substrates have the requirement of temperatures to grow a ferrite having low microwave loss. There is a great interest in fabricating the thin films of Ba-hexaferrites with either out of plane or in plane magnetic anisotropy using both amorphous or crystalline substrate for magnetic recording devices [17]. In the previous work, thin film deposition is performed usually at higher substrate temperatures, ranging from 500 to 920 °C [14,18,19]. In this paper, we present the work on the barrium hexa ferrite films deposition using KrF Excimer laser comparitively at lower substrate temperature, i.e., RT to 400 °C on Si (1 0 0) substrate.

Aim of this work is to investigate the effect of lower (<500 °C) substrate temperature on the induced parallel magnetic anisotropy, structural, morphological and optical properties of thin films.

2. Experimental setup

The Ba-hexaferrites thin films have been fabricated on Si (1 0 0) substrates using PLD technique at different substrate temperatures i.e., RT, 100, 200, 300 and 400 °C. The experimental setup is shown in Fig. 2. Prior to the deposition, the native Si oxide was removed by a standard HF etching. KrF excimer laser ($\lambda=248$ nm, 50 mJ) operated at the repetition rate of 20 Hz was focused on the target with the help of a 20 cm focal length lens. The sintered target was mounted at an angle of 45° with respect to the laser beam. The target was rotated with the help of stepper motor at 6 rpms for the uniform film deposition. Substrate was placed parallel to the target at an optimized distance of 1.5 cm. The substrate temperature was measured with a thermocouple positioned in the middle of the substrate holder. The base pressure of the chamber was attained up to 10^{-5} Torr with a turbomolecular pump.

Crystal structure of these films was investigated by X-ray diffractometer (XRD), PANAlytic Xpert in θ-2θ configuration (CuK_α line $\lambda=1.54$ Å). The surface morphology and composition of thin films was explored by the Scanning Electron Microscope (SEM), S-3400N Hitachi equipped with Energy Dispersive X-ray (EDX) spectroscope. In order to characterize the magnetic behavior of the thin films, the measurements were performed using 7400 Lake Shore Vibrating Sample Magnetometer (VSM). Film thickness and optical band gap energies were evaluated by the Ellipsometric Spectroscopy (SE).

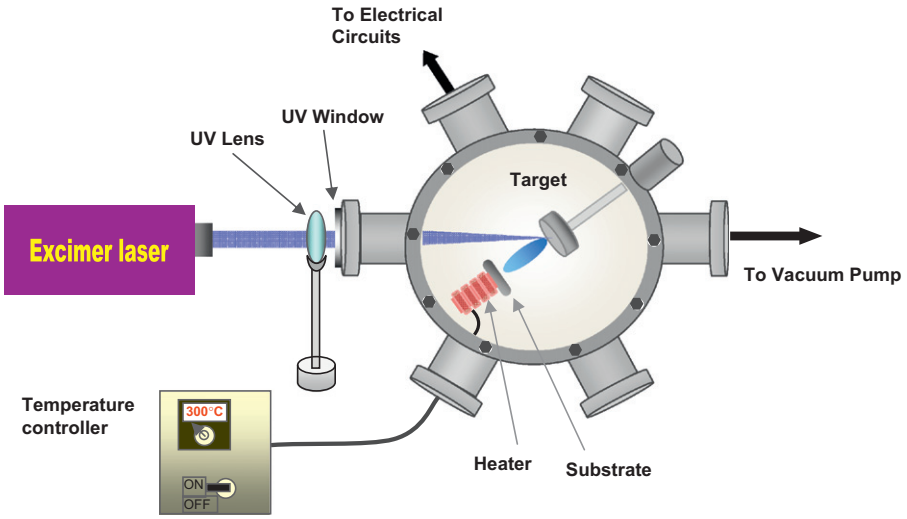

Fig. 2. Schematic of experimental setup.

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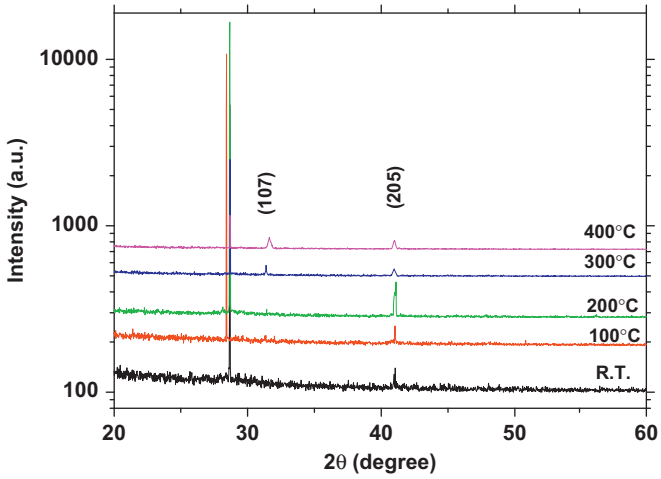

Fig. 3. XRD micrographs of Ba-Hexaferrite thin films deposited at different substrate temperatures.

3. Results and discussions

The deposited Barium hexaferrite thin films on Si (1 0 0) were characterized by XRD, SEM, VSM and Spectroscopic Ellipsometry. The obtained data are discussed in detail.

3.1. Crystallography analysis

Fig. 3 is a XRD pattern of Ba-hexaferrite thin films on silicon substrate deposited at various substrate temperatures. The film deposited at RT to 200 °C exhibits a single peak having very low intensity. These films show the amorphous structure due to insufficient substrate temperature or it may be due to the presence of some impurity phases. This leads the paramagnetic behavior of these films. The XRD pattern of the film deposited at 300 °C and 400 °C exhibits two peaks (107) and (205), respectively, having very low intensity. These films are not completely amorphous but it has a poor and insufficient crystallization of thin films [14]. Comparatively higher intensity of (107) peak as compared to (205) predicts the dominance of this plane [20,17]. Due to the higher substrate temperature, the mobility of the atoms of the growing material is higher, which is responsible for the creation of the new planes in the film. Further increase in the substrate temperature (>500 °C) might result into the formation of new planes as already reported in [14,18].

3.2. Surface morphology

Microstructures and thickness of the deposited films observed by the Field Emission Scanning Electron Microscope (FESEM) are shown in Figs. 4(a–e) and 5, respectively. The features of the films are obviously dependent on the substrate temperature. The particle size ranges from 50 to 80 nm for the films grown at RT and 100 to 150 nm for the film at 100 °C (4a and b). At these temperatures, ions, electrons or particles while residing on the substrate have low mobility [21] and thermal equilibrium is reached much faster, resulting in a very small grain growth. For the films deposited at 200 °C bigger grains are observed (4c) in the range from 50 to 200 nm, which are formed due to the increased mobility of the atoms or molecules. As the temperature is increased up to 300 °C small particles seem to be combined to form the nanorod-like morphology (4d) similar to the structures already reported in literature [22,23]. When the substrate temperature is increased up to 400 °C, it appears that nanorods diffuse with each other forming well separated bigger grains (4e) in the range from 500 nm to 1.5 μm. As the substrate temperature increases the density of the thin film increases due to the reduction of empty spaces in the growing film and as a result the thickness increases up to 500 nm (observed by FESEM). To explain the changes in the surface morphology of the thin films, due to increase in substrate temperature, following equation can be considered [23],

$$\gamma = \gamma^{o}[1-T/T_c]^{n} \quad (1)$$

where γ is the surface energy at temperature T and γ^{o} is the surface energy at critical temperature T_c. The surface energy of the substrate reduces as the temperature rises, which results in the reduction of the strength of molecule–substrate interactions. Consequently, intermolecular π–π interactions become significant. Since the high substrate temperature will cause diffusion, the adsorbed molecules are formed due to the lattice mismatch between target and substrate [24]. The Ba-hexaferrite molecules will stack-up in certain nucleation sites, which will be arranged in nanorods-like structures (for film at 300 °C) and then in circular grains (at 400 °C). The relative spacing between the particles of the film decreases as a result the thickness of the thin films increases, which is observed from the cross-sectional views in Fig. 5.

3.3. Magnetic properties

The in-plane and out-plane hysteresis loops were measured at room temperature by applying the magnetic field parallel and perpendicular to the film plane. Due to the extremely low value of magnetic moment, the hysteresis loops were obtained after subtracting the offset background signals as a function of field. The magnetic curves of the thin films deposited at different substrate temperatures are shown in Fig. 4(f–j). The applied magnetic field was swept from -10 to $+10$ KOe. The coercive force (H_c), remnant magnetization (M_r) and magnetic moment (M), as well as the hysteresis squareness ($Sq=M_r/M_s$) for in plane measurements are listed in Table 1.

The loops in Fig. 4 shows that the thin film deposited at RT, 100 and 200 °C exhibits paramagnetic behavior it may be due to the amorphous nature of the thin films. Whereas, the films prepared at 300 and 400 °C show the ferromagnetic behavior with the in-plane saturation magnetization. The saturation magnetization increases with the increasing thickness of the films. In the loops, one observes a uni-axial anisotropy with the magnetic easy axis aligned parallel to the film plane where the hard axis remained in the perpendicular direction of the film plane. The film deposited at 400 °C has small in-plane saturation magnetization i.e., 62 emu/cc and high coercivity value due to the higher thickness and larger grain shown in FESEM results. The lower value of M_s is possibly due to the insufficient crystallization of the thin films.

A simple comparison between microstructures allows us to conclude that the origin of the higher in-plane magnetization in Ba-hexaferrites with the increasing substrate temperature is associated with the texturing of the films such that the crystallographic c-axis of the individual grains lies in the film plane considering large magnitude of the magnetocrystalline anisotropy field rather than the shape anisotropy. Such confirmation is supported by the analyses of [25,26].

3.4. Optical properties

Optical band gap energy (E_g) and thickness of these thin films were determined by employing the Ellipsometery Spectroscopy using Cauchy Uruck model [27]. The optical band gap is estimated from absorption coefficient,

$$\alpha = 4\pi k/\lambda \quad (2)$$

where k is an extinction coefficient and λ is a wavelength of incident beam. According to the Tauc relation [28],

$$\alpha h\nu = A(h\nu - E_g) \quad (3)$$

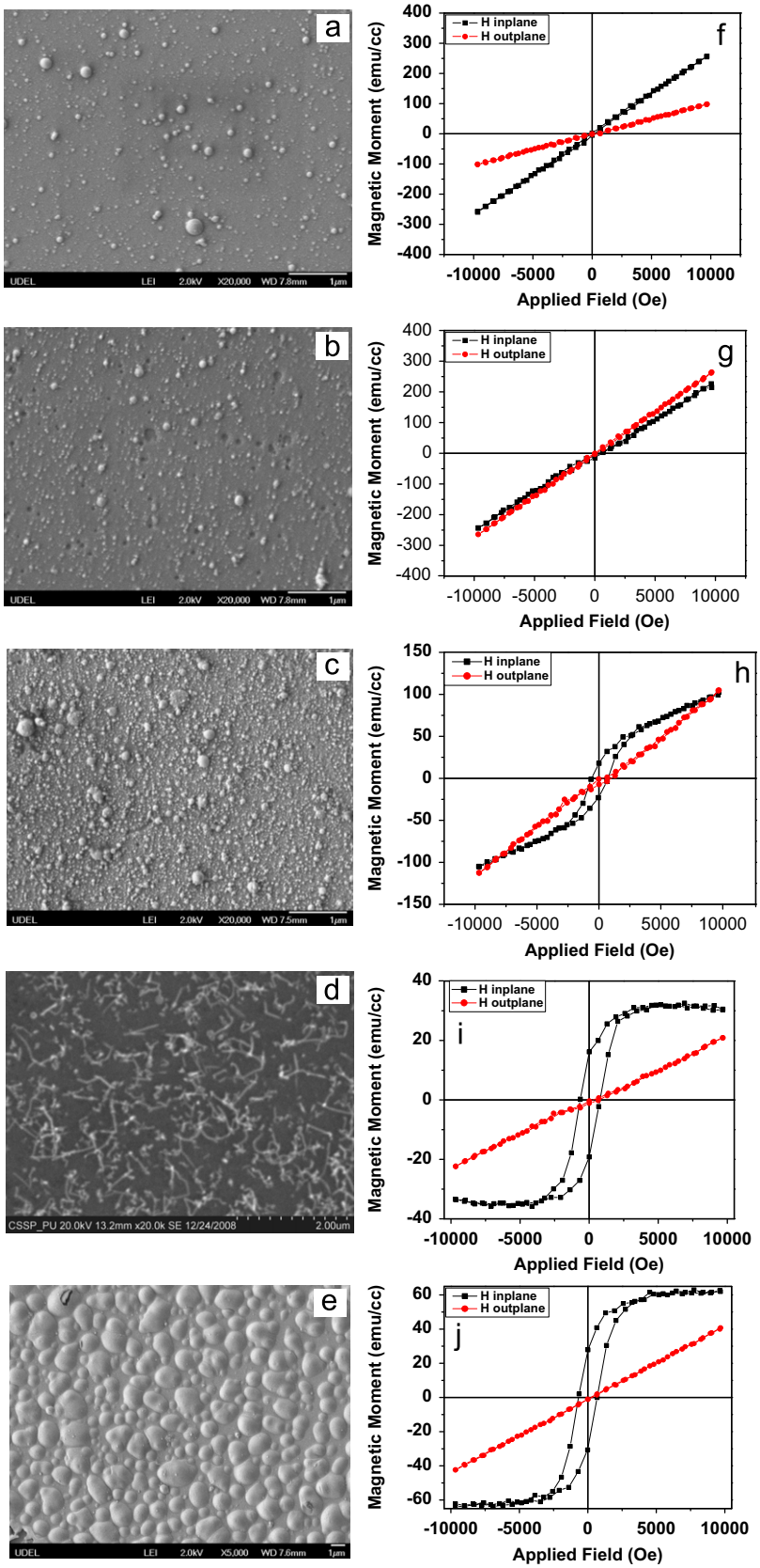

Fig. 4. SEM images of thin films deposited at (a) RT (b) 100 °C (c) 200 °C (d) 300 °C and (e) 400 °C and In-plane and out plane magnetic measurements of thin films at (f) RT (g) 100 °C (h) 200 °C (i) 300 °C and (j) 400 °C.

where A is a constant, which is different for different material, $h\nu$ is energy of incident photon, E_g is the band gap energy, and m is theoretically equal to 2 (1/2) and 3 (3/2) for allowed indirect (direct) and forbidden indirect (direct) electronic transition, respectively. $(\alpha h\nu)^2$ is plotted versus $h\nu$ as shown in Fig. 6 (for films deposited at RT and 400 °C). The extrapolation of straight

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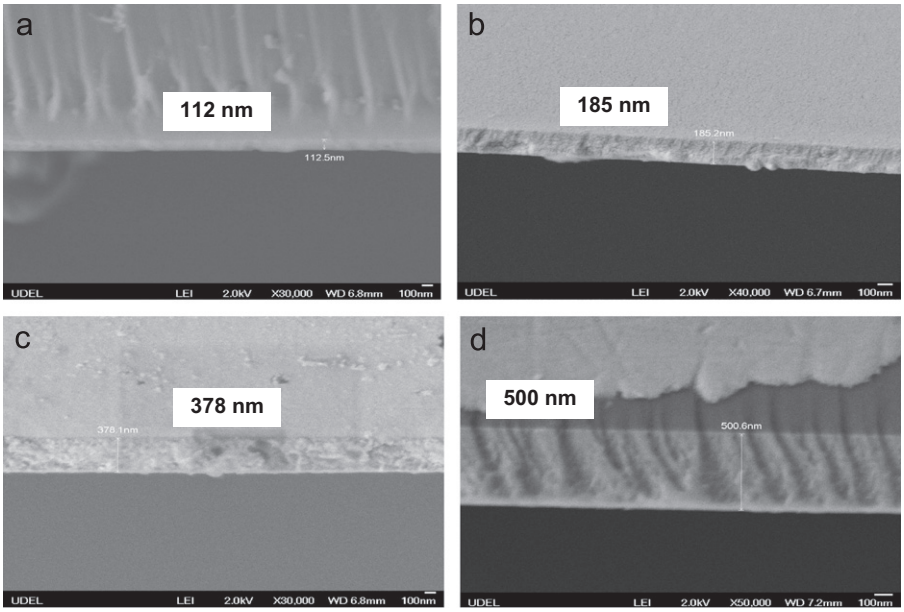

Fig. 5. Cross-sectional view of the thin films deposited at (a) 100 °C (b) 200 °C (c) 300 °C and (d) 400 °C.

Table 1
Magnetic measurement of the thin films.

Substrate temperature (°C)	Coercivity H_c (0) $\|H_c$	Moment M (emu/cm^3) $\|M_s$	M_r emu/cc	Squareness $\|M_r/M_s$
R.T.	46.25	paramagnetic	—	—
100	126.04	paramagnetic	—	—
200	619	paramagnetic	17	0.08
300	638	31	16	0.51
400	694	62	27	0.45

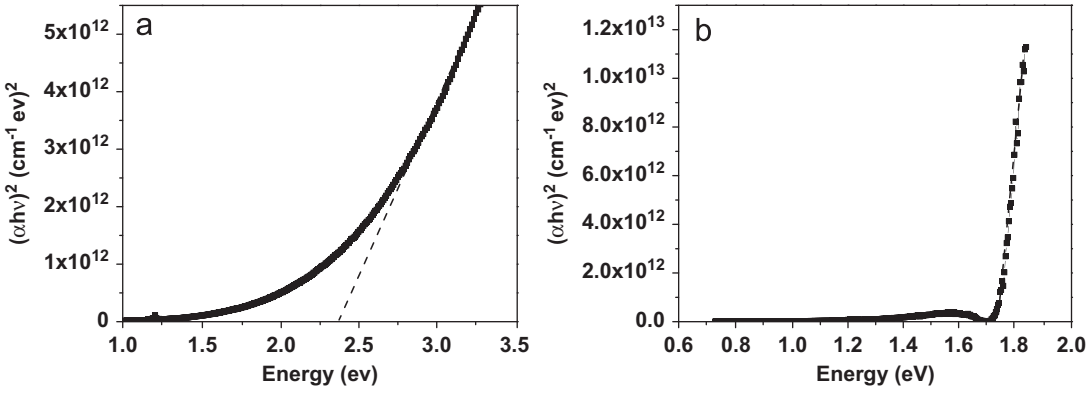

Fig. 6. Optical band gap energy of thin films at (a) RT and (b) 400 °C.

line to $(\alpha h\nu)^2=0$ gives the value of direct band gap. The estimated value of optical band gaps are 2.32 and 1.75 eV for the films deposited at RT and at 400 °C, respectively. The optical band gap energies of these films decrease as the substrate temperature increases. The thin films thickness increases from 112 to 500 nm with the increase in the substrate temperature from RT to 400 °C, respectively. This is because of the increased adhesion between hot substrate and deposited material [29]. The increase in thickness and grain size with the increasing temperature is responsible for the reduction in optical band gap energy [30].

4. Conclusions

The thin films of Ba-hexaferrites were deposited on silicon (1 0 0) substrates using the pulsed laser deposition technique at different substrate temperatures. The film deposited at 400 °C is polycrystalline, but has the insufficient film crystallization. The thickness of the film increases with the increase in the substrate temperature, which in turn is responsible for the growth of bigger grains. The in-plane anisotropy is observed at lower substrate temperature (<5 0 0). The growth temperature of 400 °C resulted

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in larger grain size and thicker films, as well as relatively high coercivity and saturation magnetization. The decrease in the band gap energy at this substrate temperature is due to the growth of larger grain and more defects inside the film.

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