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Effect of deposition temperature on structural, surface, optical and magnetic properties of pulsed laser deposited Al-doped CdO thin films

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ABSTRACT

The objective of this work is to study the influence of deposition temperature on structural, surface, optical and magnetic properties of the Al doped CdO thin films prepared by pulsed laser deposition (PLD) technique. KrF excimer laser (λ = 248 nm, τ_l = 20 ns, ν = 10 Hz, ϕ_l = 2.5 J/cm^2) was employed for the deposition of thin films. It is observed by XRD results that films grown at room temperature and 100 °C show preferential growth along (1 1 1) and (2 0 0) directions while high temperatures (200–400 °C) lead to preferential growth along the (2 0 0) direction only. The optical constants (n, k, α, and optical band gap energy) of films measured by spectroscopic ellipsometry show strong dependence upon deposition temperature. M–H loop of films, measured by vibrating sample magnetometer, deposited at 25 °C and 100 °C show paramagnetic nature while films deposited at temperatures (200–400 °C) exhibit ferromagnetic character. Scanning electron micrographs show degraded elongated grains at lower deposition temperatures, while smooth and compact surface is observed for films deposited at higher deposition temperatures.

1. Introduction

When short and high power laser pulses are focused onto the surface of a target material, a fraction of the laser pulse energy is absorbed resulting in heating, melting, vaporization and plasma formation of the material. The removed material forms a thin film upon condensing on the substrate surface under suitable conditions. The whole process is called pulsed laser deposition (PLD). PLD can be successfully employed to many classes of materials such as metals, semiconductors, dielectrics, ferroelectrics, electro-optic and giant magneto-resistance oxides, organic materials, polymers, magnetics, composites etc. [1]. Phase pure and doped CdO thin films exhibit some extraordinary properties due to which they are popular in various semiconducting, optoelectronic industries, and for the fabrication of IR mirrors, thin film resistors, low emissive windows etc. [2–8]. Deposition parameters in PLD process play key role in determining various properties of CdO thin films. Gupta et al. reported the effect of deposition parameters on various properties of Sn, Ti, Al and In doped CdO films prepared by PLD technique [9–13]. To our knowledge, the effect of deposition temperature on optical constants by spectroscopic ellipsometry (SE) and magnetic properties by vibrating sample magnetometer (VSM) of Al doped CdO has not been studied yet. In this work, influence of deposition temperature on structural, surface, optical and magnetic properties of Al–CdO thin films has been studied.

2. Experimental

2 at.wt.% Al-doped CdO target for PLD was prepared by solid-state reaction method. Required amounts of 99.99% pure CdO and Al_2O_3 were weighed by micro-electrical balance and mixed thoroughly using a fine quality mortar and pestle, then heated in air using electric furnace (Ogawa Seiki Co. Ltd. Japan) at 850 °C for 12 h. The grinding was done again and then powder mixture was cold pressed at 5 tons load using hydraulic press. The pellets were then sintered in oxygen at 900 °C for 12 h. The density of the pellets was 82% of the original density of CdO unit cell.

KrF excimer laser (Ex50, GAM LASER INC, USA) of wavelength 248 nm, pulse length 20 ns, repetition rate 10 Hz and fluence 2.5 J/cm^2 was tightly focused by 20 cm UV lens onto Al-doped CdO target at an angle of 45° from the target normal inside PLD chamber. P-type, single crystal, one side polished silicon (1 1 1) substrates of size $1 \times 1 \times 0.2$ cm^3 were ultrasonically cleaned in acetic acid and acetone; and placed at a distance of 50 mm to the target surface. The PLD chamber was evacuated down to base pressure of $\sim 10^{-5}$ mbar by rotary and turbomolecular pumps. Target holder was rotated and translated to avoid the formation of different structures on the target surface, which helps in uniform ablation along with smooth surface profile of target. Target was irradiated with 6000 laser shots to deposit thin films. The thin films of Al-doped CdO were deposited at four different temperatures. i.e. 25, 100, 200, 300 and 400 °C. Schematic of the experimental setup used for PLD is show in elsewhere [14]. The thickness of the films was found to be 200 ± 5 nm by ellipsometric method.

Structural analysis of thin film was done by X-ray diffractometer (XRD), surface morphology by scanning electron microscope (SEM), optical and magnetic properties were investigated by spectroscopic ellipsometer (SE) and vibrating sample magnetometer (VSM) respectively.

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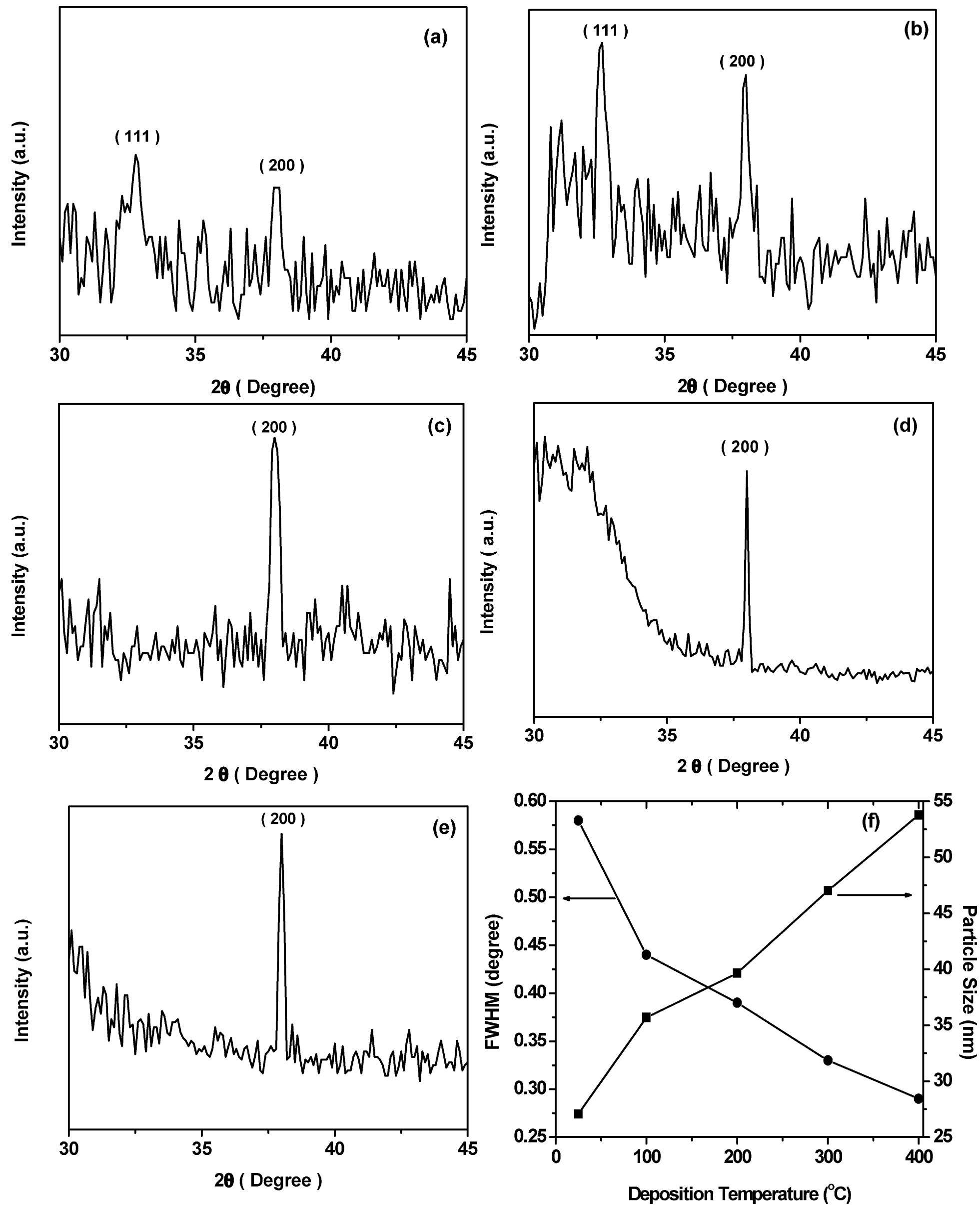

Fig. 1. XRD patterns of Al-doped CdO films grown at (a) 25 °C, (b) 100 °C, (c) 200 °C (d) 300 °C, (e) 400 °C and (f) variation of FWHM and particle size of CdO (2 0 0) as a function of temperature.

3. Results and discussion

3.1. Structural characterization

The structural characterization was done with X-ray diffractometer (D8 Discover, Bruker, Germany). The diffraction patterns of Al-doped CdO thin films grown under different deposition temperatures are shown in Fig. 1. The films grown at room temperature and 100 °C show growth along (1 1 1) and (2 0 0) planes (polycrystalline), while the films grown at higher temperatures (200–400 °C) show preferential growth along the (2 0 0) direction only (single crystal like structure). The 2θ of peaks are in good agreement with JCPDS X-ray file data. No extra peaks due to addition of aluminium in cadmium oxide films were observed, which indicates the absence of any other phase in the films. The planar density of (2 0 0) plane of single CdO unit cell (2-lattice points) is higher than that of (1 1 1) plane (1.875-lattice points). Hence, CdO (2 0 0) plane exhibits lower surface energy. Hence the evolution of sharper and intense (2 0 0) plane at higher deposition temperatures (200–400 °C) reveals that the deposition and growth was done in effective state of equilibrium. The CdO (2 0 0) peak becomes sharper, intense and reduced full width at half maximum (FWHM) with increasing deposition temperature depicting highly oriented CdO thin films with improved crystallinity.

The average X-ray particle size (D) can be determined using Scherrer's formula from FWHM [15]

$$D = \frac{k\lambda}{\beta\cos\theta} \tag{1}$$

Here the constant k is the shape factor ≈0.94, λ is the wavelength of the X-rays (1.5406 Å for CuK_{α}), θ is the Bragg's angle, and β is the FWHM. The particle size increases with increasing deposition temperature as shown in Fig. 1. The amount of defects can be estimated by calculating the dislocation line density (δ) which is related to particle size (D) as

$$\delta = \frac{1}{D^2} \tag{2}$$

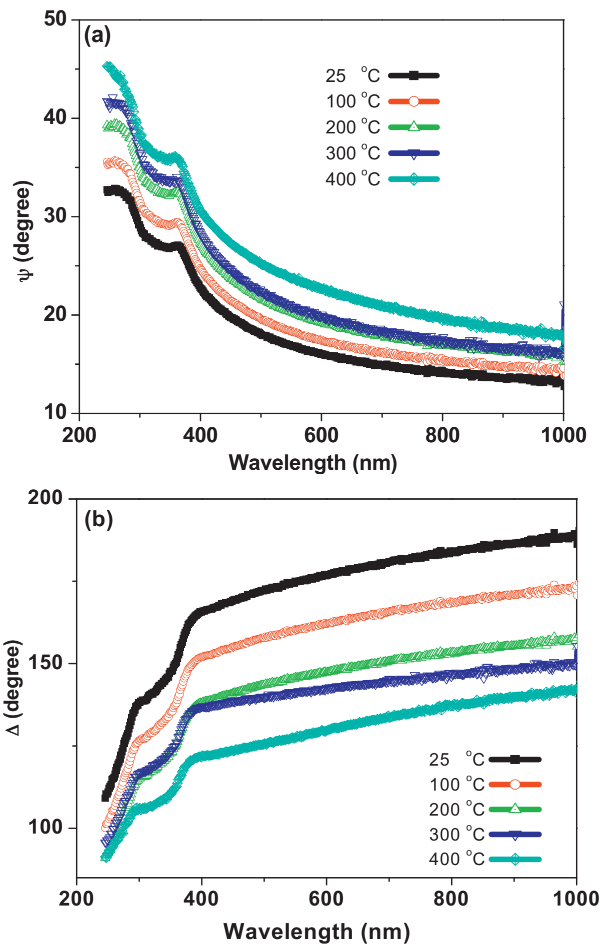

Fig. 2. SE parameters ψ (a) and Δ (b) of Al-doped CdO thin films deposited at different temperatures.

From this relation, it is obvious that as the particle size increases, the dislocation density decreases. In our case, as the deposition temperature increases, the dislocation line density decreases depicting the reduction of defect density, which implies improved crystallinity.

3.2. Optical characterization

Spectroscopic ellipsometry is an optical measurement technique, which measures the change in polarized light upon light reflection from the sample. This technique is well known and widely adaptable in material science due to high precision, non-destructive nature, fast measurement, and ability to measure the optical constants of many classes of materials. Ellipsometry measures the two values ψ and Δ, which represent the amplitude ratio and phase difference between light waves known as p- and s-polarized light waves. These values are related to the ratio of Fresnel reflection coefficients, R_p and R_s for the p- and s-polarized light, respectively [16]

$$\tan\psi \exp(i\Delta) = \frac{R_p}{R_s} \tag{3}$$

The ψ and Δ spectra as a function of wavelength for Al–CdO thin films deposited at different temperatures are shown in Fig. 2. The measurements were taken at 75° angle of incidence in air at room temperature in a wavelength range of 246–1000 nm. The measured values were best fitted using Cauchy's model. All curves show almost same trends in ψ and Δ with respect to wavelength and at different deposition temperatures.

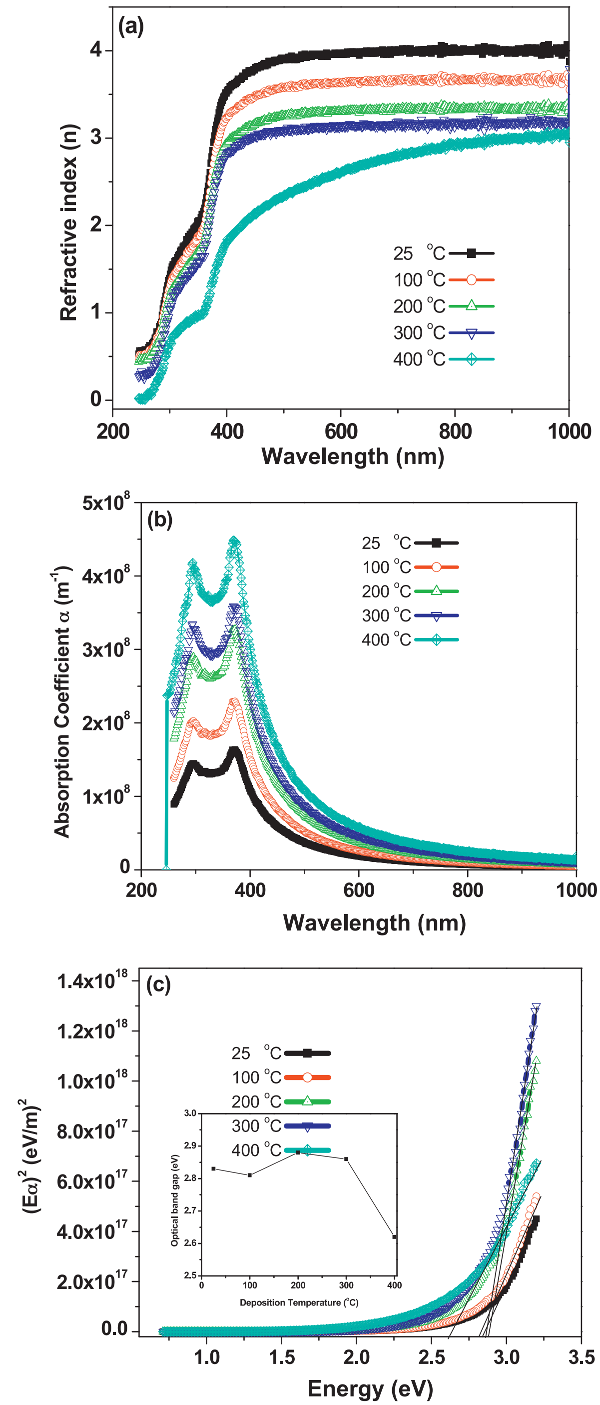

Fig. 3. Refractive index (a), absorption coefficient (b) as a function of wavelength, and plots of $(\alpha h\upsilon)^2$ versus $h\upsilon$ (c) of Al-doped CdO thin films deposited at different temperatures.

The optical constants are used to define the interaction of light with material. The complex refractive index of the optical constant of a material is represented by [16]

$$\mathrm{N} = n - ik \tag{4}$$

The real part or refractive index n describes the phase velocity of light in the medium.

The wavelength dependence of real part of "N", refractive index (n) of Al–CdO films at different deposition temperatures is shown in

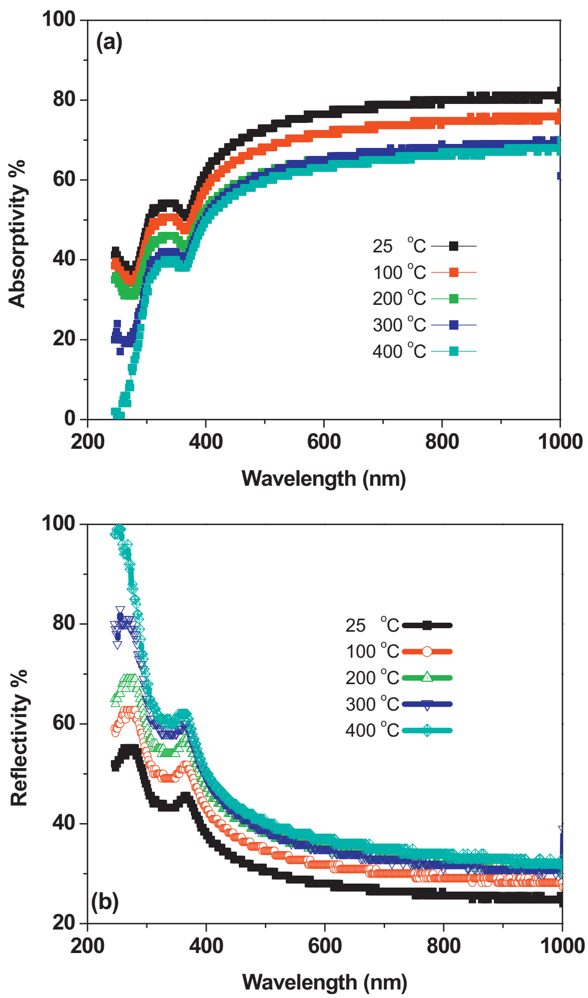

Fig. 4. Absorptivity (a) and reflectivity (b) as a function of wavelength for Al-doped CdO thin films deposited at different temperatures.

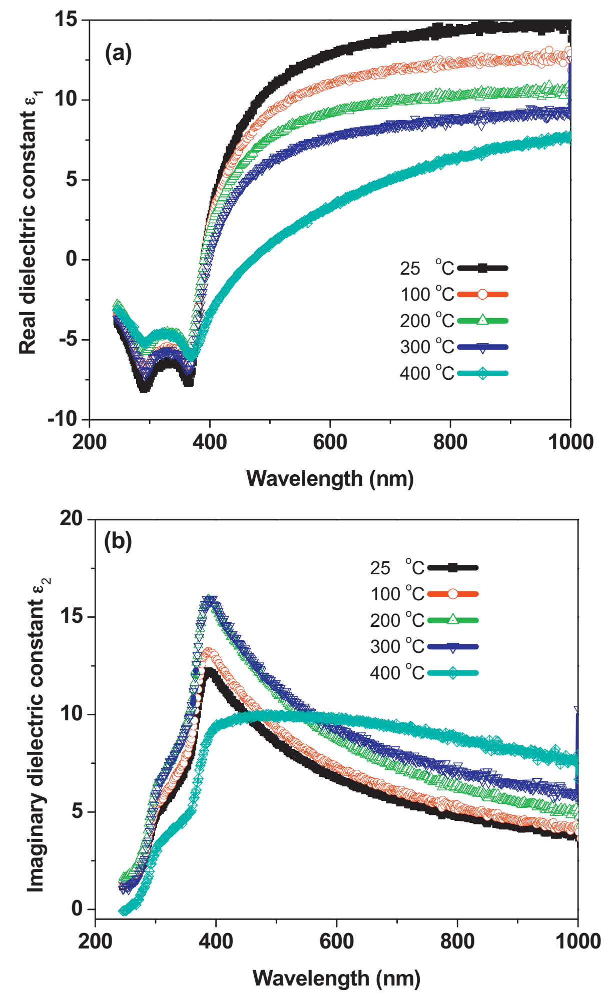

Fig. 5. Plot of real (a) and imaginary (b) parts of dielectric constants as a function of wavelength for Al-doped CdO thin films deposited at different temperatures.

Fig. 3a. It is observed that refractive index of all deposited thin films first increases from 200 nm to 400 nm, and then stagnates from 400 nm to 1000 nm. But due to increase in growth temperature, it starts decreasing from room temperature to 400 °C. All deposited thin films show the same trend at different temperatures.

The imaginary part of complex refractive index or extinction coefficient "*k*" defines a measure of the extent by which the intensity of a beam of light is reduced by passing through the material. Using formula $\alpha = 4\pi k/\lambda$, the variation of absorption coefficient (α) as a function of wavelength of Al–CdO thin films at different growth temperatures is shown in Fig. 3b. All curves show two peaks from 200 nm to 400 nm, then start decreasing monotonically from 400 nm to 1000 nm, suggesting transparent behaviour in IR region. All the films show the same trend of absorption coefficient (α) as a function of wavelength. It is also evident from the figure that the absorption coefficients of the deposited thin films increase with the increase in growth temperature.

The CdO is a material with direct band gap lying in the range of 2.2–2.7 eV [17]. For such band to band transitions, the dependence of absorption coefficient α versus photon energy is given by the relation [16]

$$(\alpha h\nu)^2 = A\,(h\nu - E_g) \tag{5}$$

where A is a parameter independent of $h\upsilon$ and E_g is the optical band gap energy. Plotting the graph of $(\alpha h\upsilon)^2$ versus $h\upsilon$, the value of E_g can be determined by extrapolating the linear portion of this plot to $(\alpha h\upsilon)^2 = 0$. The extrapolation of plots of $(\alpha h\upsilon)^2$ versus $h\upsilon$ of Al-doped CdO thin films at different growth temperatures is shown in Fig. 3c. It is obvious from the figure that the optical band gap of the deposited thin films is shifted to lower energy when they are deposited at higher temperatures. The obtained values of optical band gap energy of Al-doped CdO thin films are from 2.8 eV to 2.6 eV. When electromagnetic radiation stikes a surface, some part is reflected, some is absorbed and some is transmitted. The reflectivity and aborptivity of thin film are calculated by using values of "*n*" and "*k*" using following relation

$$R = \frac{[(n-1)^2 + k^2]}{[(n+1)^2 + k^2]} \tag{6}$$

$$A = 1 - R \quad \text{(For opaque materials)} \tag{7}$$

$$A = \frac{4n}{[(n+1)^2 + k^2]} \tag{8}$$

Fig. 4 shows absorptivity "*A*" and reflectivity "*R*" of Al-doped CdO thin films at different deposition temperatures. Fig. 4a shows maximum absorption at $\lambda > 400$ nm, which decreases as wavelengths decreases. It is evident from Fig. 4b that thin films show maximum reflectivity at shorter wavelengths and it decreases monotonically with increase in wavelength. It can also be seen that reflectivity increases and absorptivity decreases with increase in thin film growth temperature.

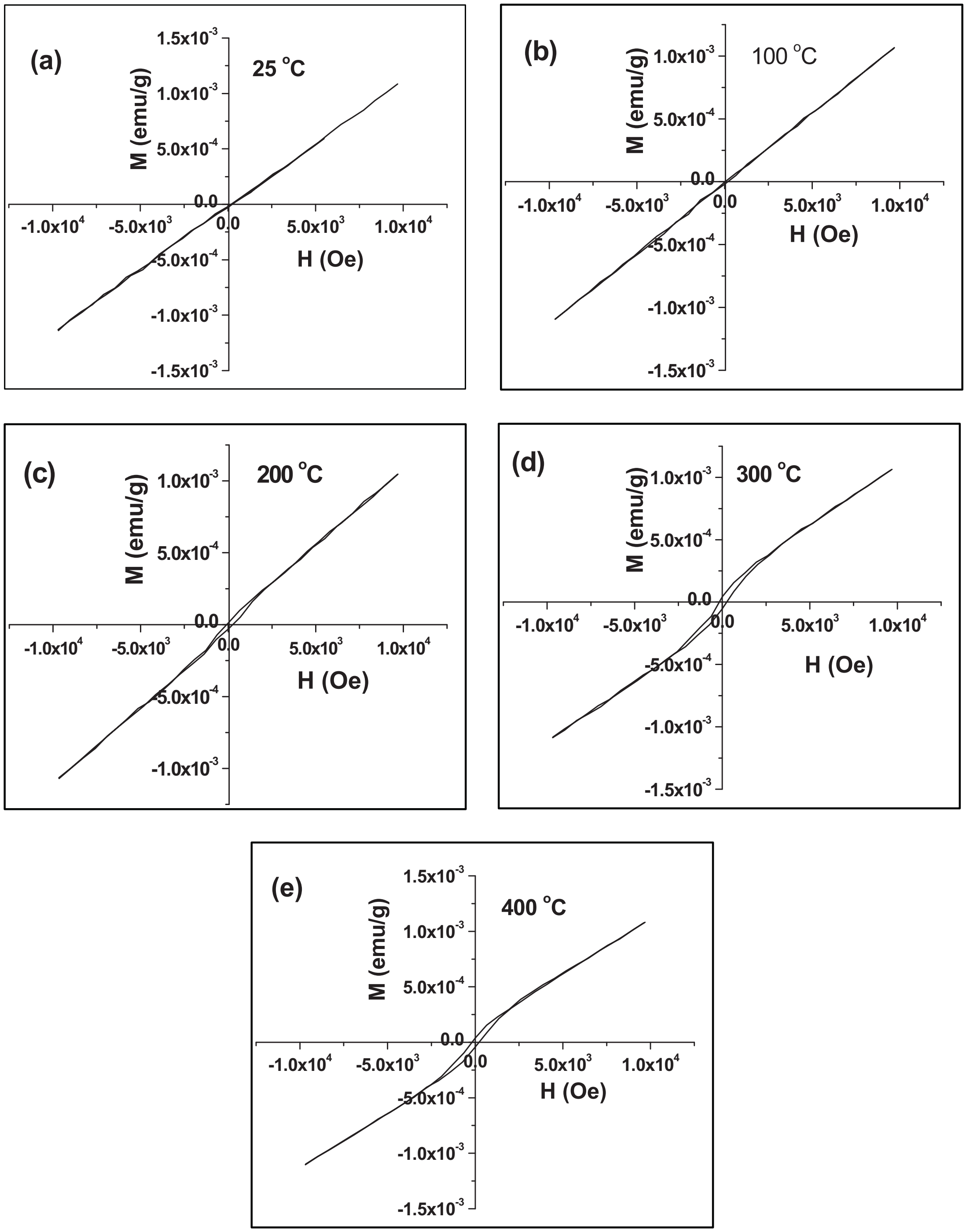

Fig. 6. Magnetization loop of Al-doped CdO thin films deposited at (a) 25 °C, (b) 100 °C, (c) 200 °C, (d) 300 °C, and (e) 400 °C.

Free electrons in metals and free carriers in semiconductors absorb light and alter dielectric functions. The Drude's model has been applied widely to describe such light absorption [16]. The complex dielectric constant (ε) is define as

$$\varepsilon = \varepsilon_1 - i\varepsilon_2 \quad (9)$$

So according to the Drude's theory, the real (ε_1) and imaginary (ε_2) parts of the complex dielectric function can be expressed as

$$\varepsilon_1 = n^2 - k^2 \quad (10)$$

$$\varepsilon_2 = 2nk \quad (11)$$

Using the above equations the real and the imaginary part of complex dielectric constant of Al-doped CdO deposited films at different growth temperatures were calculated and plotted in Fig. 5 as a function of wavelength.

It can be seen in Fig. 5a that the real dielectric constant is less in UV region. Then it starts increasing from 400 nm to 700 nm and then stagnates up to 1000 nm. All the films show same trend. However, the real part of dielectric constant shows decreasing trend as the growth temperature increases. Fig. 5b shows the imaginary part of dielectric constant of all deposited thin films at different growth temperatures. All curves show the maximum peak at 380 nm and then they start decreasing as the wavelength increases. It is also evi-

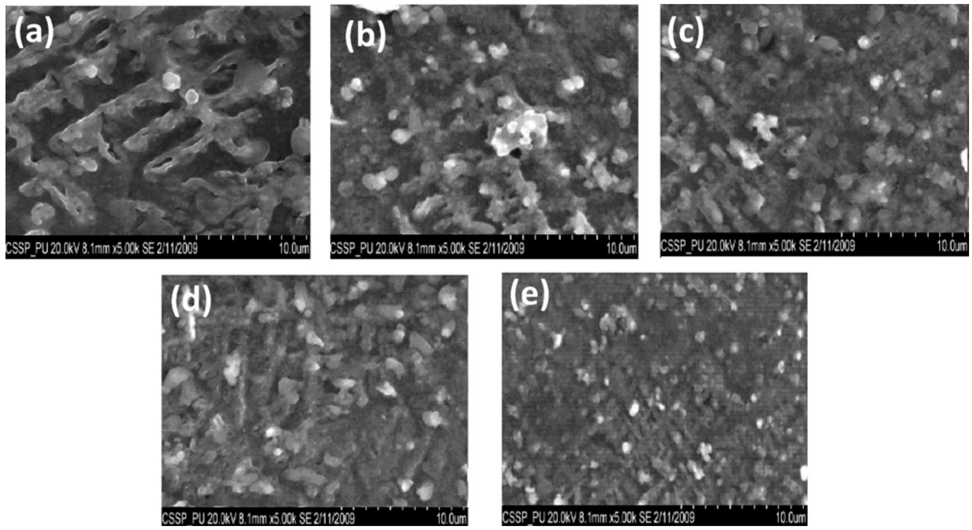

Fig. 7. SEM images of Al-doped CdO thin films deposited at (a) 25 °C, (b) 100 °C, (c) 200 °C, (d) 300 °C, and (e) 400 °C.

dent from the figure that ε_2 increases with the increase in growth temperature of the films.

3.3. Magnetic characterization

Vibrating sample magnetometer (Lakeshore 7407) is used to investigate the magnetic properties of Al-doped CdO thin films on silicon substrate at different growth temperatures.

Fig. 6a–e shows the M–H loops of the deposited thin film at room temperature, 100 °C, 200 °C, 300 °C and 400 °C respectively. It is evident from the figure that the M–H loop of film deposited at 25 °C and 100 °C show paramagnetic nature while films deposited at temperatures (200–400 °C) exhibit some ferromagnetic character. It is clear from the figures that area of hysteresis loop of the deposited thin films is increasing with increase in growth temperature. The paramagnetic nature of films appears due to presence of aluminium. The emergence of ferromagnetic character in Al–CdO thin films at higher deposition temperatures is possibly due to single crystal like growth in (2 0 0) direction.

3.4. Surface morphology

The surface morphology of doped CdO thin films significantly influence their various properties due to which they play a key role in many applications linked to optoelectronics [18]. The morphological microstructure of Al-doped CdO thin films deposited at different substrate temperatures was studied by SEM (Hitachi 3400 N) and is shown in Fig. 7. It is obvious from the figure that all the films comprise of different shaped microcrystallites and grains. At low substrate temperature, the sputter particles absorbed on the surface of the substrates and forms degraded elongated grains. At high substrate temperature, the atoms get more energy from the substrate and move longer with more diffusion on the surface. Hence, uniform surface with dense microstructure can be seen for the films deposited at high deposition temperature, which is also indicating improvement of the crystal quality with increasing temperature as depicted by XRD patterns. The presence of holes at the film surface also makes the surface rough. Some particulates of different sizes and shapes are present, which are inherently linked to pulsed laser ablation process. The average SEM particle size for films deposited at 25 °C, 100 °C, 200 °C, 300 °C and 400 °C was 1.91 μm, 1 μm, 0.84 μm, 1 μm and 0.3 μm respectively. The roughness was measured by atomic force microscope. The roughness of films deposited at 25 °C, 100 °C, 200 °C, 300 °C and 400 °C were found to be 22 nm, 12 nm, 10 nm, 9 nm and 2.5 nm respectively confirming SEM results that films become smoother as deposition temperature increases. Many mechanisms like surface boiling, exfoliation, thermal and hydrodynamic sputtering and splashing may be involved in particulate generation [19].

4. Conclusions

In this research work, Al-doped CdO thin films were deposited by PLD technique on silicon (1 1 1) substrate. The effect of deposition temperature on structural, surface, optical, magnetic properties was studied. The XRD patterns show that deposition temperature affects the preferential growth of the films. The films deposited on unheated substrate and 100 °C has (1 1 1) and (2 0 0) orientations. While the films grown at higher temperatures (200–400 °C) show preferential growth along the (2 0 0) direction only. The spectroscopic ellipsometry results show the deposition temperature effects on optical properties of deposited thin films. The extinction coefficient (k), refractive index (n), and optical band gap energy (E_g), absorptivity, reflectivity, real dielectric constant (ε_1), imaginary dielectric constant (ε_2) of the deposited films vary with deposition temperature. The deposition temperatures also show some interesting effect on magnetic properties of the deposited films. M–H loop of films deposited at 25 °C and 100 °C show paramagnetic while films deposited at temperatures (200–400 °C) exhibit ferromagnetic character. The remanance and coercivity are also found to vary with deposition temperature. Scanning electron micrographs show degraded elongated grains at lower deposition temperatures, while smooth and compact surface is observed for films deposited at higher deposition temperatures. The present results show that the optical and magnetic properties can be modulated by varying the deposition temperature. The film, which is deposited at 400 °C, show only (2 0 0) orientation with least value of FWHM, smooth surface morphology, lowest band gap and ferromagnetic character. These films with such band gap values and ferromagnetic character have potential applications in optoelectronics and spintronics.

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