



Dispersion Parameters of Thermally Deposited Thin Lithium Fluoride Films at Different Annealing Temperatures

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Abstract

Thin Lithium Fluoride films have been prepared by thermal evaporation technique on glass substrate under vacuum of about 10^{-5} mbar. The thickness of the films was $4000 \pm 50 \text{ \AA}$. The effects of annealing temperatures on the optical properties and dispersion parameters have been studied. Transmittance spectra of the films indicate that the films have high transparency. The optical absorption studies reveal that the transition is direct with band gap value varied with the annealing temperatures. Also the refractive index dispersion curves obey to the single oscillator's model. The dispersion energy and single-oscillator energy varied with the annealing temperatures

Keywords: Thin LiF Film, Thermal Evaporation, UV-VIS Spectrum, Single Oscillator Model

معلومات التفريق لأغشية فلوريد الليثيوم الرقيقة المرسبة حرارياً لدرجات تليدين مختلفة

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الخلاصة

حضرت اغشية فلوريد الليثيوم الرقيقة بتقنية التبخير الحراري على ارضية من الزجاج تحت ضغط بحر 5-10 ملي بار. وكان سمك الاغشية 4000 ± 50 انكستروم. تم دراسة تأثير التليدين على الخصائص البصرية ومعلومات التفريق للاغشية المحضرة. اثبت طيف النفاذية بان الاغشية تمتلك نفاذية عالية. اظهرت دراسات معامل الامتصاص بان الانتقال في هذه الاغشية هي من النوع المباشر وكانت فجوة الطاقة تتغير مع درجات التليدين. كذلك تم ملاحظة ان منحنى معامل الانكسار يتبع موديل التذبذب المنفرد. لوحظ ان طاقة التفريق وطاقة التذبذب المنفرد تتغير مع درجات التليدين.

1.Introduction

Lithium fluoride (LiF) belongs to the family of alkali halides (salt of hydrofluoric acid) and appears as white solid powder forming an ionic crystal with the cubic rock salt structure. The bulk lattice parameter is about 4.03 \AA . The two involved elements lithium and fluoride have the smallest radius between alkali and halide ions. The cation-anion distance is 1.5639 \AA , the smallest for alkali halides which is caused by the fact that fluorine has the largest electron affinity amongst all elements. It is a molarity mass 25.94 g/mol with density $\rho = 2.635 \text{ g/cm}^3$ and the melting point is $845 \text{ }^\circ\text{C}$ a very good electrical insulator and transparent to short wavelength ultraviolet (UV) radiation due to its high band gap with interesting applications in integrated optics and specialized UV optics [1, 2]. Lithium fluoride is of special technological and scientific interest because of some of its special features. Thin coatings of LiF can reduce the work function of metal electrodes significantly enhancing electron injection and field emission in semiconductor devices [1]. Reversible hardening of lithium fluoride crystals by irradiation and post heating as well as the production of color centers has been reported [1, 3]. The ability of forming color centers, induced by ionizing radiation, pushes LiF in the focus for applications

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in optoelectronics [1]. Lithium fluoride has the lowest refractive index of all common infrared materials. It also possesses the highest UV transmission of any material. It is slightly soluble in water, while being soluble in hydrofluoric acid (HF) and other acids. However, it can be cleaned with alcohol. Lithium fluoride is most widely used as a flux in the production of near infrared camera (NIRCam), Webb space telescope (WST) in its lenses, enamels, glasses and glazes [4, 5]. Similarly it is also used in brazing and welding fluxes and molten salt chemistry in metallurgy, and it is also used for X-ray monochromator plates as an analysis crystal, used as a target to produce X-ray [6] heat sink materials and UV transmission windows include specialized UV optics and as a means to record gamma and neutron exposure in thermoluminescent dosimeters [1].

2. Experimental

LiF thin films supplied from Flibe company were deposited by Edward E306A vacuum system under high vacuum of about 10⁻⁵mbar on 7059 corning glass slides substrate kept at room temperature. Molybdenum boat was used as a source. Prior to deposition on glass substrates (size: 75×25×1.35 mm³) were cleaned ultrasonically with acetone and demonized water and finally air dried. The as-deposited films were annealed at 373, 423 and 473 K annealing temperatures using Memert vacuum oven of 10⁻³mbar vacuum. The thicknesses (t) of the prepared films were measured using fizue method which is 4000±50Å. The optical absorption has been measured by using a double beam UV-VIS spectrophotometer type Perkin-Elmer Lambda 900. Transmittance (T) and Reflectance (R) sprctra at room temperature was recorded in the wavelength range 300-900 nm. The effect of annealing temperatures on the optical properties and dispersion parameters of LiF thin films were studied. The optical absorption has been measured after each annealing process.

3. Results and Discussion

The absorbance spectrum (A) for LiF thin films with different annealing temperatures reveals that the films have low absorbance in visible /near infrared region from 350nm to 850nm as puplished in this reference [7]. The trancemittance and reflectance spectra of LiF thin films on glass substrate at different annealing temperatures 373, 423 and 573 K have been illustrated in Figure-1.

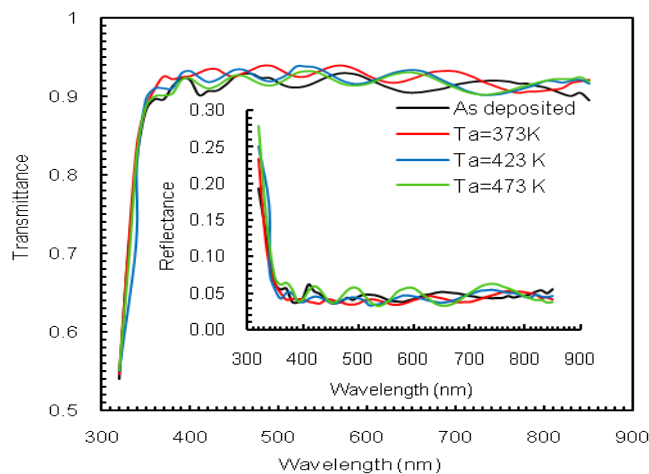


Figure 1-The transmittance and reflectance spectra as a function of wavelength of as deposited and annealed thin LiF films at different annealing temperatures.

Analysis of optical Absorption spectrum is one of the most productive tools for understanding of the band structure and energy band gap (E_g) of the crystalline structure. It can be observed from this figure that the absorption coefficient of the LiF films is characterized by strong absorption at the shorter wavelength region between 320-850 nm. In the shorter wavelength the absorption coefficient exhibits high values of absorption coefficient (α) $>10^4$ cm⁻¹ which means that there is a large probability of the allowed direct transition [8], and then absorption coefficient decreases as wavelength increases. In general, it can be observed that the absorbance decreases with increasing the annealing temperature. The shifts of absorbance spectrum to longer wavelength (smaller energies) compared to that of the annealed films for all samples, may be attributed to crystallinity improvement by increasing the annealing temperature [9], similar behavior have found by Hadi et al [8]. The spectral dependence of absorption coefficient in the strong absorption region ($\alpha \propto 10^4$ cm) is given by Tauc equation [10]:

$$\alpha h\nu = B (h\nu - E_g)^r \tag{1}$$

Where B is energy independent constant and r is equal to 2 or 1/2 for allowed indirect or direct transitions, respectively. A good fit between the experimental data for prepared films when r=1/2. It is well known that direct transition across the band gap is feasible between the valence and the conduction band edges in k space. In this transition process, the total energy and momentum of the electron-photon system must be conserved [illican et al 2008]. The values of the direct optical band gap (E_g) values of the LiF thin films were obtained from the intercept of $(\alpha h\nu)^2$ as function of photon energy ($h\nu$) curves plotted as shown in Figure-2, their values are given in Table-1. The values of the energy gap increased by annealing because of the annealing process could decrease the disorder present in the structure then reduce the tail states, which lead to increase optical energy gap.

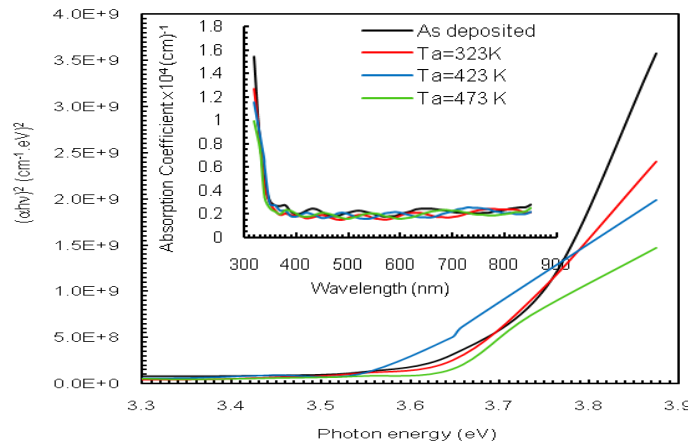


Figure 2-The variation of $(\alpha h\nu)^2$ with photon energy and the absorption coefficient as a function of wavelength of thin LiF films at different annealing temperatures.

In order to determine the absorption band edge of the as deposited and annealed LiF films, we computed the first derivative of optical transmittance and are presented in Figure-3.

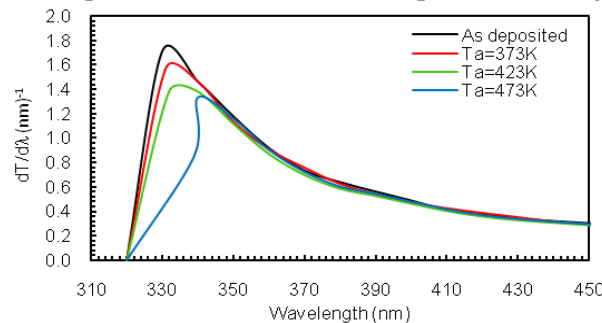


Figure 3- The variation of $dT/d\lambda$ as a function of wavelength of the as deposited and annealed thin LiF films at different temperatures.

The plots of $dT/d\lambda$ as a function to the wavelength give a peak corresponding to the absorption band edge. The peak position of the curves shifts to longer wavelengths with increased the annealing temperature. The absorption wavelength values corresponding to the peak positions for the prepared films varied from 329 to 341 nm. This suggests that the absorption band edge shifts from 3.19 to 3.08 eV with increased the annealing temperature. The increased the annealing temperature is accompanied by a systematic low-energy shift of the band gap extending down to the yellow spectral range. The width of localized states inside the optical band gap of the LiF films is called Urbach tail, which is related directly to a similar exponential tail for the density of states of either one of the two band edges. The Urbach tail of the films can be determined by the following relation [11]:

$$\alpha = \alpha_0 \exp\left(\frac{h\nu}{E_u}\right) \tag{2}$$

Where $h\nu$ is the photon energy, α_0 is constant and E_u is Urbach energy which refers the width of the exponential absorption edge and it gives information about localized state in the band gap. Figure-4 shows the variation of $\ln\alpha$ as a function of photon energy for the LiF thin films. This behavior

corresponds primarily to optical transitions between occupied states in the valence band tail to unoccupied states at the conduction band edge. Urbach energy value was calculated from the reciprocal of the slope of the linear part of Figure-4, which give the value of E_u .

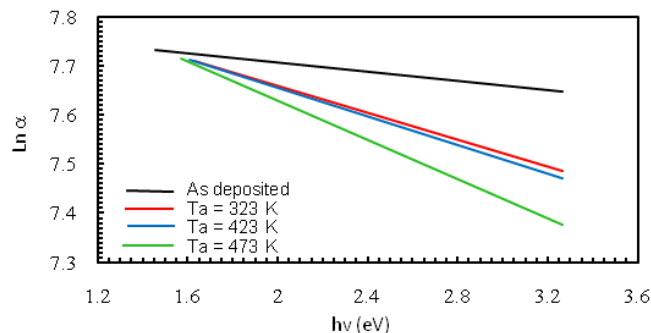


Figure 4-The variation of $\text{Ln}\alpha$ as a function of photon energy for LiF thin films

The values of Urbach energy are given in Table-1. The E_u values of the films have decreased with increasing the annealing temperature, which is may be due to recrystalezation of films structure. The dependence of the optical absorption coefficient with photon energy may arise from electronic transitions between localized states [2008]. The density of these states falls off exponentially with energy which is consistent the theory of Tauc [10], so that equation 1 can be rewritten as the following:

$$\alpha = \alpha_0 \exp\left(\frac{\beta}{k_B T}\right) E \tag{4}$$

Where, β is called the steepness parameter, which characterizes the broadening of the absorption edge due to the electron–phonon interaction or exciton–phonon interaction, k_B is Boltzman constant and T is the absolute temperature. If the width of the edge is related to the slope of equation 4, the β parameter is found as $\beta = (k_B T/E_u)$, which is calculated by using this relationship. The absolute temperature is taken at room temperature and different annealing temperatures as tabulated in Table-1. The steepness parameter values suggest that the absorption edge changes as annealing temperature changes. The refractive index dispersion plays an important role in optical communication and designing of the optical devices, so that it is important to determine dispersion parameters of the films. Because of the dispersion energy is related to the optical transition strengths and optical conductivity. Thus, in order to analyze the refractive index dispersion of the films, we used the single-oscillator model, developed by Didomenico and Wemple [12]. In terms of the dispersion energy (E_d) and single-oscillator energy for electronic transitions (E_o), the refractive index at a frequency can be expressed. The single-oscillator model for the refractive index dispersion is expressed as follows [12]:

$$(n^2 - 1) = \frac{(E_d E_o)}{[(E_o)^2 - (h\nu)^2]} \tag{5}$$

Where n is the refractive index. The dispersion energy which is a measure of the strength of inters band optical transitions. This model describes the dielectric response for transitions below the optical gap. Plotting $(n^2-1)^{-1}$ versus $(h\nu)^2$ allows us to determine the oscillator parameters. The dispersion energy and single-oscillator energy values were calculated from the slope and intercept on the vertical axis of $(n^2-1)^{-1}$ as a function of $(h\nu)^2$ plot and figure 5 illustrates $(n^2-1)^{-1}$ as a function of the square of photon energy $(h\nu)^2$. The dispersion energy and single-oscillator energy values are tabulated in Table-1, they are increase With increasing the annealing temperature.

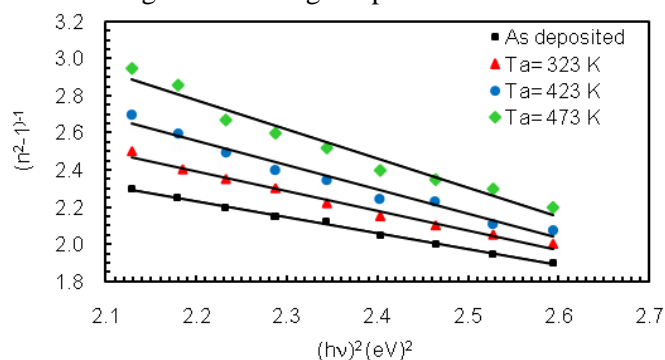


Figure 5-The variation of $(n^2-1)^{-1}$ as a function of the square of photon energy for LiF thin films.

The single-oscillator parameters and dispersion energy are related to the imaginary part of the complex dielectric constant (ϵ_r) [13]. The parameter includes the desired response information about electronic and optical properties of the material. The M-1 and M-3 moments of the optical spectrum can be obtained from the following relations [14]:

$$E_0^2 = \frac{M_{-1}}{M_{-3}} \quad (6)$$

$$E_d^2 = \frac{M_{-1}^2}{M_{-3}} \quad (7)$$

The M-1 and M-3 moments of the optical spectrum values have decreased with increasing the annealing temperature as shown in Table-1. The refractive index n_1 at infinite wavelength can be determined by the following relation [15]:

$$\frac{n_{\infty}^2 - 1}{n^2 - 1} = 1 - \left(\frac{\lambda_0}{\lambda}\right)^2 \quad (8)$$

The plot of $(n^2 - 1) - 1$ vs. λ^{-2} was plotted to obtain n_{∞} value of LiF thin films. The n_{∞} values were found to be decreased with increasing the annealing temperature as given in Table-1.

Table 1-Some optical and dispersion parameters of as deposited and annealed thin LiF films at different annealing temperatures.

Annealing temperature (K)	E_g (eV)	$B \times 10^9$ (cm ⁻¹)	E_u (eV)	$\beta \times 10^{-3}$	E_o (eV)	E_d (eV)	M_{-1}	M_{-3} (eV) ⁻²	n_{∞}
As deposited	3.55	0.7	21.74	1.15	0.860	4.13	4.80	6.40	2.96
373	3.57	0.9	7.25	4.44	1.064	4.30	4.47	3.94	2.71
423	3.59	4.0	6.89	5.29	1.303	5.42	4.40	3.90	2.48
473	3.65	6.0	5.05	8.08	1.574	6.24	3.94	1.59	2.30

4. Conclusion

The prepared films have more than 88% transparency in the visible region, and optical band gap of the films was found to vary from 3.55 up to 3.65 eV. Urbach energy of the films changes inversely with optical band gap. The refractive index dispersion curve of LiF thin film obeys the single-oscillator model. The dispersion energy and single-oscillator energy for as deposited films were found to be 0.86 eV and 4.125 eV respectively and increased up to 1.54 eV and 6.239 eV respectively after annealing at 473 K.

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