A probe into compositional and structural dependence of optical properties of lanthanum fluoride films prepared by resistive heating

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The paper describes investigations into the correlation between the optical properties and the composition, structure and morphology of lanthanum fluoride films deposited at 373–473 K substrate temperatures by resistive heating of lanthanum fluoride powders. The composition of the films that includes depth profiling of fluorine has been determined non-destructively by ion beam analysis while their structure and morphology have been investigated by glancing incidence X-ray diffraction and atomic force microscopy respectively. The films are polycrystalline, exist in hexagonal phase and display substrate temperature dependent texturing. The substrate temperature has an important influence on composition as well. The films deposited at 373 K or 398 K substrate temperatures are deficient in fluorine but tend to acquire stoichiometric composition at 473 K. Possessing granular (∼100 nm) morphology, the films, in general, are UV transparent but their optical loss increases with texturing. Carbon and oxygen, present as impurities, lower the density and consequently the refractive index (1.47) of the films. Annealing in vacuum at 573 K brings about deterioration in the optical properties of the films which are related mainly to morphological changes and thermal stress.

1. Introduction

Lanthanum trifluoride (LaF$_3$) has evoked immense interest among researchers due to its unique structural, electrical and optical properties. Existing in hexagonal lattice with tysonite structure, LaF$_3$ exhibits high ionic conductivity (∼10^{-6} S/cm) which makes it an eminently suitable candidate material for sensor applications [1–5]. The extensive use of LaF$_3$ membranes in ion selective electrodes for the determination of fluoride ions is a testimony of its potential for such applications [6]. Good chemical stability is another important merit of the compound which, recently has been exploited to improve the electrochemical characteristics of LiCoO$_2$ thin films [7]. In terms of optical properties, LaF$_3$ is endowed with a band gap of about 10.3 eV and its transmission range spans from 130 nm to 10 μm wavelength region. In fact, it is one of the few materials that are used for ultraviolet (UV), deep ultraviolet (DUV) as well as vacuum ultraviolet (VUV) coatings [8–10]. In addition, the compound has a refractive index of about 1.6 and it displays good anti reflecting properties as well.

The present report deals with the optical properties of LaF$_3$ films prepared at different substrate temperatures by resistive heating (RH) of LaF$_3$ powders. Among physical vapour deposition techniques, RH is known to produce LaF$_3$ films with the least optical loss [11]. Investigations on the structural and compositional features of the films are the two other major aspects of the present study and an attempt has been made to correlate them with the preparative conditions and the optical properties of the films. Compositional analysis that also involves depth profiling of fluorine, has been performed non-destructively by ion beam analysis (IBA) techniques namely proton elastic backscattering spectrometry (p-EBS) and proton induced γ-ray emission (PIGE). It assumes significance since there is a considerable scatter in the data on the atomic ratio of La to F (N_{La}:N_F) and the relative content of oxygen, an ubiquitous impurity, in LaF$_3$ films in literature [4,12–15]. In most of these studies, analytical measurements have been performed by X-ray photoelectron spectroscopy in combination with sputtering. However such measurements are prone to large errors due to the preferential removal of fluorine atoms. Therefore analysis by non-destructive techniques is desirable to get a better insight into the deposition process and the functionality of the coatings. Finally, even as the results are discussed in terms of optical properties, since the structural and compositional features of the films are inherent to the deposition and processing

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conditions, these investigations are relevant to the other areas of application as well.

2. Experimental details

2.1. Deposition and annealing of films

The films were deposited on soda lime glass and fused silica substrates at a rate of 1–2 Å/s by resistively heating LaF_3 powder (99.9%, Acros Organics) in a Ta-boat at $\sim2 \times 10^{-4}$ Pa vacuum in a thermal evaporation unit. Vacuum in the deposition chamber was created and maintained by an oil diffusion pump (with a liquid nitrogen trap) backed by a rotary pump. The substrates were initially cleaned ultrasonically in isopropanol and were subsequently sputter cleaned in situ in Ar plasma. The distance between the boat and the platen onto which the substrates were fixed was about 70 mm. The platen rotated at 25 rpm to ensure uniform deposition. The films were deposited on substrates heated to 398 K or 473 K by radiation heaters which measured ~450 nm in thickness. Films were also deposited on substrates that were not intentionally heated. However, these experienced heating by the radiation from the Ta-boat during the course of depositions. To discriminate the influence of substrate temperature (T_S) on the properties of the films, ~260 nm films were deposited which resulted in the rise of substrate temperature to about 373 K at the end of the process and are referred to as prepared at T_S = 373 K. After deposition the specimens were allowed to cool down naturally in the vacuum chamber to about 300 K and stored separately under mild static vacuum for further processing or examination. The films on fused silica were annealed at 573 K in vacuum (7×10^{-3} Pa) for 2 h in a quartz tubular furnace pumped by a turbomolecular pump. The annealed films were removed from the furnace at about 300 K.

2.2. Characterization

2.2.1. Phase evolution

The phase evolution in the films was examined by glancing-incidence X-ray diffraction (GI-XRD) (incidence angle = 1°; step size = 0.1°; scan speed = 1° per minute) by a Rigaku (Ultima IV) diffractometer using Cu K_α radiation (λ = 1.5402 Å).

2.2.2. Compositional analysis by IBA and methodological considerations

Films, pristine as well as those annealed in vacuum, were depth profiled for fluorine by PIGE, employing the resonance at 872 keV in $^{19}F(p, \alpha\gamma)^{16}O$ nuclear reaction [16]. The measurements were accomplished by bombarding the films at normal incidence with a well collimated proton beam in energy steps of 2 keV beyond the resonance energy and measuring 6.1, 6.9 and 7.1 MeV γ-rays, characteristic of the reaction, by high purity Ge (HPGe) detector at each step. In addition, EBS experiments using 2.0 MeV proton beam were also conducted to ascertain the impurities prevailing in the films. The experiments involved the bombardment of films at normal incidence with proton beam and the detection of the particles scattered at 170° angle by a Si-surface barrier detector. The choice of beam energy and scattering angle is governed primarily by considerations of mass resolution. As described later, these measurements show that C and O are the two discernible impurities present in the films. Therefore, the films symbolise a quaternary compound and can be represented by a chemical formula $LaC_pO_qF_r$.

The content (r) of fluorine (relative to La) in at a depth x in such quaternary films can be obtained by PIGE using the relationship

$$r = R \times \frac{f(\text{std})[\varepsilon(\text{La}) + p\varepsilon(\text{C}) + q\varepsilon(\text{O})]}{\varepsilon(\text{std}) - [R \times f(\text{std}) \times \varepsilon(\text{F})]} \qquad (1)$$

where f(std) is the atomic fraction of fluorine in the standard, which, in the present case, is calcium fluoride (CaF_2), R is ratio of the charge normalized yields of 6–7 MeV γ-rays for the films and the standard, ε is the stopping cross section of the element indicated in bracket or CaF_2 for 872 keV protons. The depth x (at./cm²) was calculated by the equation

$$x = \frac{(E - E_R)}{\varepsilon(\text{film})} \qquad (2)$$

where E is the incident beam energy, E_R is the resonance energy and ε(film) is the stopping cross-section of the beam in the film.

The methodology outlined above shows that a priori knowledge of the relative content of carbon (p) as well as that of oxygen (q) is essential for determining the depth profiles of fluorine in the films. Hence, these were obtained by simulating the EBS spectra by SIMNRA. The elastic cross-sections of $^{28}Si(p, p)^{28}Si$ and $^{12}C(p, p)^{12}C$ scatterings reported by Amirikas et al. [17], and those of $^{16}O(p, p)^{16}O$ scattering reported by Gurbich [18] were used in simulations. However for fluorine Rutherford scattering cross-sections were used in spite of the fact that similar to C, O and Si, F also exhibits non-Rutherford scattering under the present experimental conditions. It is to be noted that while the elastic scattering cross sections for C, O and Si have been measured by several research groups and are known with 2–3% accuracy in a wide proton energy and scattering angle range, there is a lack of corresponding data, particularly around E_p = 2.0 MeV at large scattering angles, for fluorine. The situation is further accentuated by the prevalence of a significant disagreement among the reported values which is suggestive of difficulties in accurate determination of $^{19}F(p, p)^{19}F$ scattering cross-sections. These considerations prompted us to use the Rutherford backscattering cross-sections of fluorine in simulations. The atomic compositions of the films determined by EBS measurements are thus approximate in nature and, to a rough estimate, can have about 20% error.

Since simulations provide relative quantification, an error of about 20% in F content will be reflected in the other constituents namely La, C and O of the films. We probed the influence of the errors in the contents of these elements on the depth profiles of F determined by Eq. (1) and found it to be ~6%. The uncertainty in the determination of fluorine, as such, is about ~10% which is calculated by addition in quadrature, the uncertainties in stopping cross-section (3%), charge collection (3%) and yield determination (5%) and the above mentioned uncertainty of ~6%. Meanwhile, the uncertainty in the determination of depth or areal density of a film is ~5%. It is to be noted that the stopping cross sections of the elements were calculated using Ziegler–Biersack formulations while the stopping cross sections of the films were calculated by the Bragg's rule of linear addition.

2.2.3. Optical and morphological analysis

The transmittance and reflectance of the films were measured in 200–900 nm wavelength region by a UV–Vis spectrophotometer. The refractive indices and thickness of the films were determined by the method outlined by Swanepoel [19]. It involves the creation of envelopes connecting the maxima (T_M) and minima (T_m) of the interference patterns, and the refractive index (n) and film thickness (d) can be calculated using the following equations

$$n = \left[N + (N^2 - s^2)^{1/2}\right]^{1/2} \qquad (3)$$

$$d = \frac{\lambda_1 \lambda_2}{2(\lambda_1 n_2 - \lambda_2 n_1)} \qquad (4)$$

s is the refractive index of the substrate, λ_1 and λ_2 are the wavelengths of two adjacent maxima or minima and