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The structural, optical and morphological properties of CaF_2 thin films by using Thermionic Vacuum Arc (TVA)

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ABSTRACT

In this study, calcium fluoride (CaF_2) thin films have been prepared by Thermionic Vacuum Arc (TVA) technique on glass substrates. In this technique CaF_2 thin films are produced by condensing the plasma of anode material generated in the TVA setup under high vacuum conditions on glass substrates. Crystal structures as well as optical and surface properties of CaF_2 antireflective (AR) coated thin films were investigated. X-ray diffraction (XRD) measurements showed that amorphous CaF_2 thin films were formed. Optical and surface properties of CaF_2 films have been studied based on optical transmittance, reflectance, refractive index and atomic force microscopy imaging (AFM). Our results also show that CaF_2 coated samples exhibit lower reflectance (R). From our optical studies, we have observed that CaF_2 thin films have high AR properties.

1. Introduction

Recent improvements in the optical behavior of materials such as fluorides and oxides with large band-gaps have been utilized for ultraviolet (UV) optics and in optoelectronic devices [1,2]. Especially, calcium fluoride (CaF_2) has become the most important material commercially within the optics community [3]. Antireflective (AR) coatings usually consist of a combination of materials with different refractive indices. An ultra low refractive index is very advantageous when one designs an antireflection coating [4]. CaF_2 has low refractive index. It also has a wide transmittance range approximately from 150 nm to 12,000 nm [5]. Hence, CaF_2 is used for infrared imaging systems, large-scale semiconductor photolithography systems, special window material for vacuum application, AR coatings, optical community, etc. [5].

In general, antireflection coatings on optical substrates are prepared by means of dry processes, such as vacuum evaporation or sputtering. However, it is difficult to lower the refractive index of thin films below that of the bulk material by a dry process because of their dense structure [4]. The surface quality of CaF_2 coatings is strongly dependent on optical performance. The most common purpose of AR coating is to reduce the surface reflection [3]. However, in order to enhance the optical performance of coated materials, a surface reflectance of 4% could be reduced down to about 1% in the visible region based on the material properties, the environment in which the coated surface will be operated, and sometimes the cost of production [3].

In order to produce the optical multilayer and filters, CaF_2 can be deposited as thin films using mainly physical vapor deposition (PVD) techniques such as, electron-beam evaporation (EBE) [6–9], thermal evaporation [10–12], r.f. magnetron sputtering [13], pulsed laser deposition (PLD) [14,15], and molecular beam epitaxial (MBE) [16].

In this study, we investigated the structural, optical and surface properties of CaF_2 thin films deposited on glass substrates using the TVA technique for a different technique. The TVA technique for depositing thin films utilizes a plasma discharge source which generates pure metal and non-metal plasma. The TVA discharge occurs between cathode and anode under high or ultra high vacuum conditions [17–24]. The cathode in the Wehnelt cylinder contains a heated tungsten filament which emits electrons and the anode contains the substrate material to be coated. When the accelerated electrons, due to high dc potential difference between the anode and cathode, collide with the anode they heat the anode due to kinetic energies (heat) transferred to the anode material from the high speed electrons during such collisions. Then, the heated anode material starts to melt and later evaporates. A steady state concentration of the

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evaporated atoms of anode materials is established quickly in the medium between the anode and the cathode. With further increase in the accelerating dc voltage, a bright thermionic vacuum arc occurs in the vacuum chamber due to the vaporized atoms of the anode material [17–24]. Under the suitable pressure in the vacuum chamber, the generated plasma material deposited on the substrate forms a thin film. It is possible to coat large surfaces with the TVA technique.

The advantages of the TVA according to other plasma assisted techniques have been reported as high quality, high purity, low roughness, high adhesion, and homogenous. They are also compact and nanostructured. Moreover deposition time in this technique is very short [17–24].

2. Experimental procedure

CaF_2 thin films were deposited on glass substrates using the TVA technique in a plasma assisted deposition technique, knowledge of characteristics of the plasma of the coating material is important because the quality of thin films depends on the plasma of the coating material. For this purpose, optical emission spectroscopy (OES) of CaF_2 was obtained during the deposition in the spectral range from 200 to 850 nm. The result is shown in Fig. 1. As seen in Fig. 1, peak intensities show the formation of calcium and flour atoms in plasma. To analyze the quality of the produced CaF_2 thin films, the structural, optical and surface properties have been investigated. Fig. 1 displays the optical emission spectroscopy of CaF_2 plasma where in the inset the TVA set-up with OES is also depicted schematically [24].

In our studies we have used CaF_2 as the anode material in a tungsten crucible. The main working parameters during the deposition of CaF_2 films by the TVA technique are the pressure in the vacuum chamber, which is approximately 10^{-5} Torr, the filament current in the cathode which is 18 A, and the applied voltage between the anode and the cathode which is 1 kV. Also, the deposition time is 10 min. CaF_2 thin films generated by the TVA technique are obtained under high vacuum conditions.

The crystal structure of the deposited CaF_2 thin films was analyzed by X-ray diffraction (XRD) analysis using Rigaku-rint-2200 X-ray diffractometer employing Cu-K_α radiation. The surface morphology of the film was imagined by an Ambios Q-scope atomic force microscopy device. Root mean square (RMS) of the roughness was determined by the AFM from 40 lines on imaging scale. Thickness, reflection and refractive index measurement were measured by a Filmetrics F20 device. These values were generated using Cauchy model. They have been compared with theoretical results and literature values. The theoretical results were generated by a trial optical software. Finally, a transmittance spectrum was determined with a Perkin-Elmer UV/vis Lambda 2S spectrophotometer.

3. Results and discussion

The structure of the CaF_2 films was studied using Rigaku-rint-2200 X-ray diffractometer employing Cu-K_α radiation. Fig. 2 shows the X-ray diffraction (XRD) pattern of a typical CaF_2 film in the scattering angle (2θ) ranging from 20° to70°. Since the XRD data in Fig. 2 show no sharp peaks we can conclude that our CaF_2 films were amorphous.

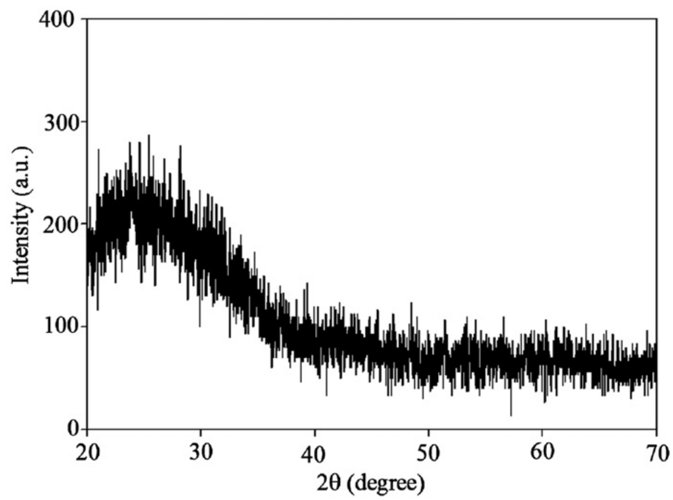

Fig. 2. The XRD patterns of CaF_2 films.

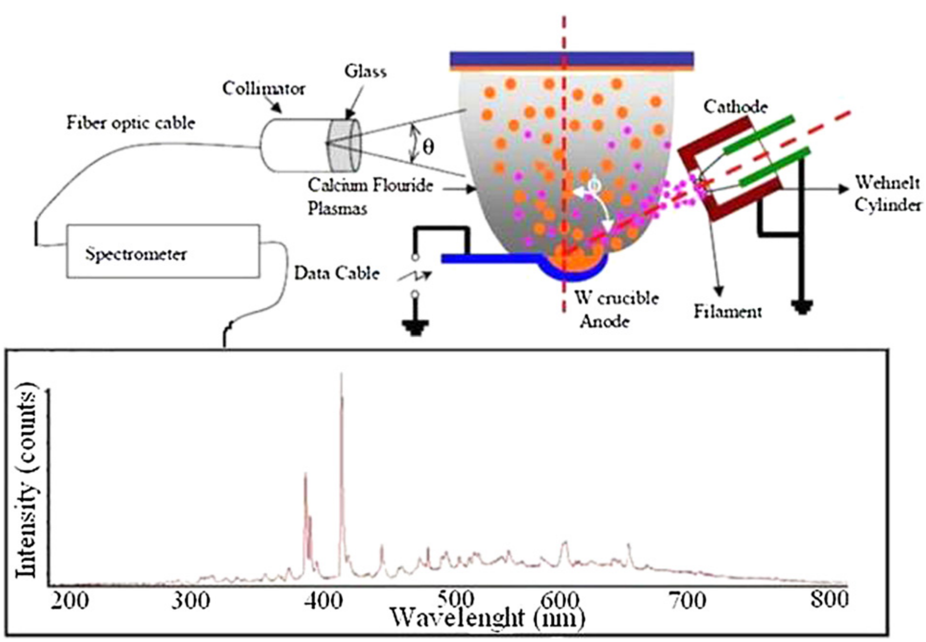

Fig. 1. OES of CaF_2 plasma and schematic view of the electrodes arrangement for TVA discharges (inset).

Fabricating films with a smooth surface is desirable since the smoothness of the film is directly related to its quality. The morphology of a CaF_2 thin film is important for AR coating. Fig. 3 shows an AFM image of such a film obtained using an Ambios Q-scope AFM device.

We have carried out root mean square (RMS) roughness calculations from the observed peak heights in the AFM data from an area of $4 \times 4\ \mu m^2$. The RMS roughness value of CaF_2 film surfaces calculated in this way was found to be 10 nm. These results show that the TVA produced CaF_2 thin films are compact, smooth, homogeneous and they possess a nanostructure which is in good agreement with the TVA literature [17–24].

Optical characteristics of the AR coatings depend on film thicknesses of coated layers, their transparencies and refractive index. A Filmetrics F20 thickness measurement system was used for thickness, reflection, and refractive index measurements. CaF_2 molecules were deposited to form a single layer antireflective (SLAR) film with approximately 100 nm thickness. To measure the transmittance of coating samples, a Perkin-Elmer UV/VIS Lambda 2S spectrophotometer was used. Transmittance spectra of the CaF_2 thin films are compared with the spectra of uncoated glass samples. Fig. 4 shows the plot of transmission and reflection as a function of wavelength for a typical CaF_2 coating. As seen from Fig. 4, the transmittance of the CaF_2 coated samples and that of the uncoated ones are approximately equal at 550 nm wavelength. The transparency of the studied CaF_2 thin film is 89% at 550 nm. The reflectance of the same CaF_2 film is very low as we expected.

It should be noted that, the refractive index depends on the film deposition method since the mass density of materials and crystal orientations will affect the refractive index. According to Lorentz–Lorenz equation, refractive index increases with rising of the film density [25]. The crystal structure of CaF_2 is cubic formation. Measured refractive index of CaF_2 thin films by Filmetrics F20 is 1.44 at 550 nm. This result is in good agreement with literature [5,25,26].The spectral dependence of the refractive index for a CaF_2 film is presented in Fig. 4.

Measured refractive index of CaF_2 thin films and refractive index of bulk CaF_2 window are compared in Fig. 4. Refractive indices of bulk CaF_2 have been taken from Ref. [27]. The data of bulk sample were generated using Sellmeier dispersion model. For the produced thin film, Cauchy model was used. These refractive index values are very close to each other in high frequency (infrared) region.

4. Conclusions

We have investigated the optical and surface properties of CaF_2 thin films produced by our TVA technique. The coating of glass substrates with CaF_2 films increased the transmittance

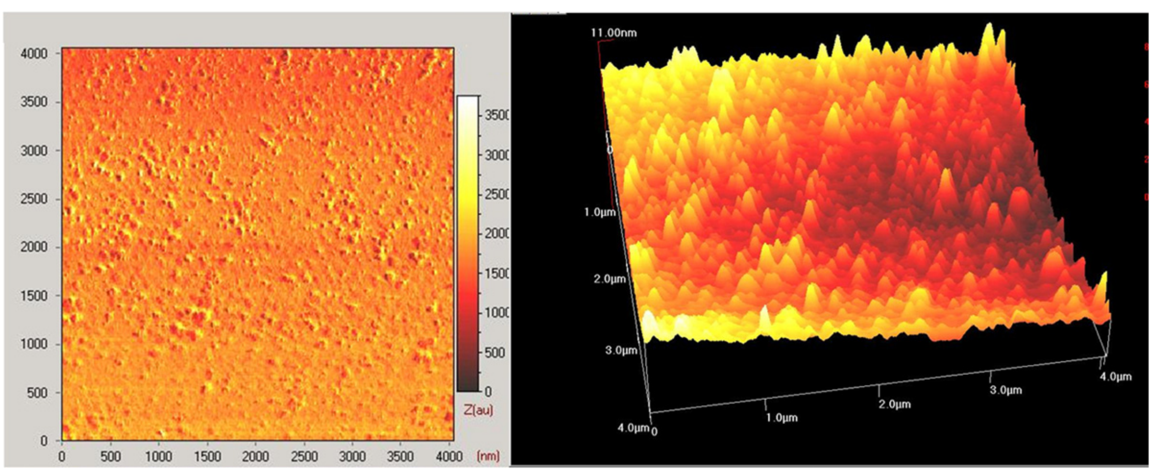

Fig. 3. AFM images of CaF_2 films.

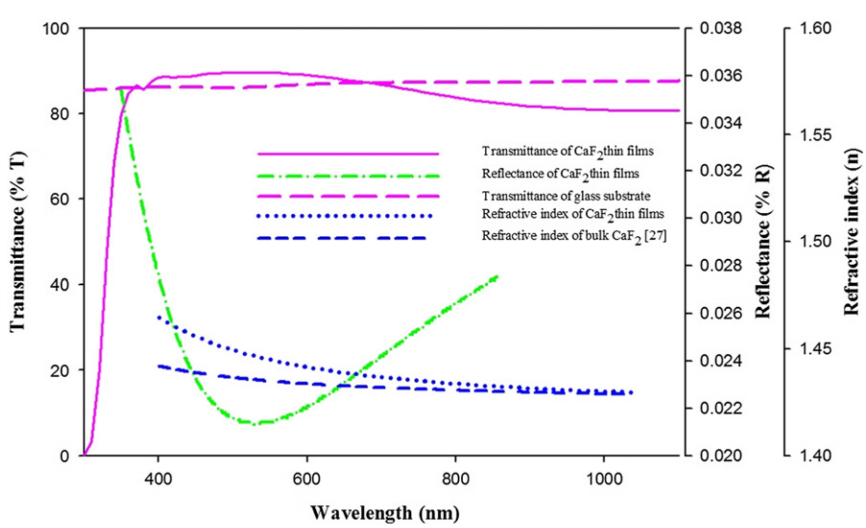

Fig. 4. Transmission and reflection spectra along with the wavelength dependency of the refractive index for a typical CaF_2 thin film sample.

compared to the uncoated glass samples and the measured refractive index values were seen to be in good agreement with the literature. Analysis of CaF_2 surfaces showed that such films produced by the TVA are smooth, homogenous and compact. Our analyses show that CaF_2 thin films produced by the TVA technique are suitable for single and multilayer AR coating. The TVA technique, to produce CaF_2 thin films, has some advantages over other techniques such as very short coating times and a good control of film thicknesses. We conclude that the TVA technique is very suitable for industrial ophthalmic applications. In addition, optically transparent CaF_2 films can be used to make optical multilayer and filters.

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