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Reactive electron beam evaporated gadolinia films at ambient substrate temperature: optical properties and morphology studies

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Abstract

Depositing optical coatings at ambient substrate temperature has been stimulating interest as it has a range of potential applications. However, developing such optical coatings especially using refractory oxides is challenging since they yield stable thin films mostly at elevated substrate temperatures. Gadolinia films (Gd_2O_3), in the present experiment, however, observed to form stable films even at ambient substrate temperatures when deposited through reactive electron beam deposition. In addition, the films exhibited interesting optical properties such as reasonably high refractive index and wide band gap, which are rarely obtainable with conventional oxide materials. During the deposition, rate and oxygen pressure have been systematically varied. The deposited films have subsequently been characterized for optical and band gap related properties using spectrophotometric as well as ellipsometric spectral measurements. Atomic force microscopy has also been employed to study the surface topography and morphological changes under various deposition conditions. Both oxygen pressure and rate of evaporation have observed to greatly influence both the optical constant and surface topography of the gadolinia films.

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Keywords: Gadolinia films; Deep UV optical coatings; Optical properties; Rare earth oxides; Optical constants

1. Introduction

Thin film refractory oxide materials such as ZrO_2, HfO_2, Sc_2O_3, MgO, Y_2O_3, etc., represent a very important group of coating materials because of their mechanical and chemical stability and their wide range of useful optical properties [1]. These are the most suitable optical material for thin film optical coating applications especially in the visible, UV and deep UV spectral regions. In most optical coating applications, reactive electron beam (EB) evaporation technique has been successfully adopted for depositing oxide thin

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films and multilayers. In such deposition process, high quality dense and stable oxide thin films are mostly obtained only when substrate is kept at elevated temperatures [1]. Nevertheless, ambient substrate temperature deposition condition is of great importance due their potential applications such as development of metal-dielectric filters and coatings on temperature sensitive substrates, etc. In this present article, we presented optical and surface properties of gadolinia films deposited at such ambient substrate temperature condition.

Rare earth oxides such as Er_2O_3, Yb_2O_3, and Eu_2O_3 have shown interesting optical properties such as high values of refractive index and good transmission down to 250 nm [2–4]. They also have interesting physical properties for use in various device applications [5]. In addition, they are characterized by a good chemical, thermal and mechanical stability [5]. Gadolinia (Gd_2O_3) is one of the rare earth oxides, which has the potential to be used in the extended spectral region including for deep UV applications. In earlier studies on gadolinia films, optical properties have been reported on films, which are deposited mostly on quartz substrate at elevated substrate temperatures [6–8]. However, in our present studies, gadolinia films are observed to form stable films even at ambient substrate temperatures. This observation indeed a contrast to the few other most widely used deep UV transmitting oxide materials, which always yield durable films only when deposited on heated substrates. In this study, gadolinia films have been deposited on quartz substrate at ambient substrate temperature while rate and oxygen pressure have been systematically varied. Optical and surface properties of these films have been characterized using UV–vis–NIR spectrophotometer, phase modulated ellipsometer and atomic force microscope (AFM). The details of the preparation and characterization results have been presented in the subsequent sections.

2. Deposition and characterization of gadolinia thin films

In this work, several samples of gadolinia thin films have been deposited using VERA 902 reactive electron beam evaporation system. Gd_2O_3 granules (Lot number: G1076) of purity 99.9%, produced by Cerac Inc. have been used as starting material. A water-cooled 8 kW electron beam gun has been used as the evaporation source. During the deposition, rate of deposition and total physical thickness have been controlled using Leybold's XTC/2 quartz crystal monitors. Besides, Leybold's OMS 2000 optical monitoring system has been used to record the optical thickness using quarter-wave-monitoring technique. MKS mass flow controllers have been interfaced with the coating system for controlling the total pressure during the reactive evaporation process. The partial pressures of reacting gases have been monitored using Pfeiffer's Prisma 200 residual gas analyzer. The gadolinia granules have been preheated and melted to remove all the trapped gases, which cause spattering of the materials, before carrying out the deposition process.

The films have been deposited on quartz substrate by keeping the substrate at ambient temperature conditions. However, rate of evaporation and oxygen pressure have been systematically varied during the deposition process. This is to study the influence of both the rate of deposition and oxygen pressure on optical properties of the gadolinia thin films at ambient substrate temperature. In the present work, the rate of deposition has been varied from 5 to 20 Å/s, whereas, the oxygen pressure has been varied from 0.5×10^{-4} to 3×10^{-4} mbar. Most of the films have been deposited with the optical thickness in the range of $7\lambda/4$ to $9\lambda/4$ ($\lambda/4$ being the quarter-wave thickness) at the monitoring wavelength (λ) of 600 nm. Subsequently, optical properties and surface topographies have been studied using spectrophotometry and atomic force microscopy. The methods of characterization and their results have been presented in the following sections.

2.1. Spectrophotometric characterization

Optical characterization of gadolinium oxide films has been carried out from spectral transmittance measurements, which were obtained through Shimadzu UV3101PC spectrophotometer. These measurements have been performed in the wavelength region from 190 to 1100 nm. Some specific films were also measured beyond 1100 nm for their transmittance as well as reflectance. The extrapolated envelope method has been employed to extract refractive index,

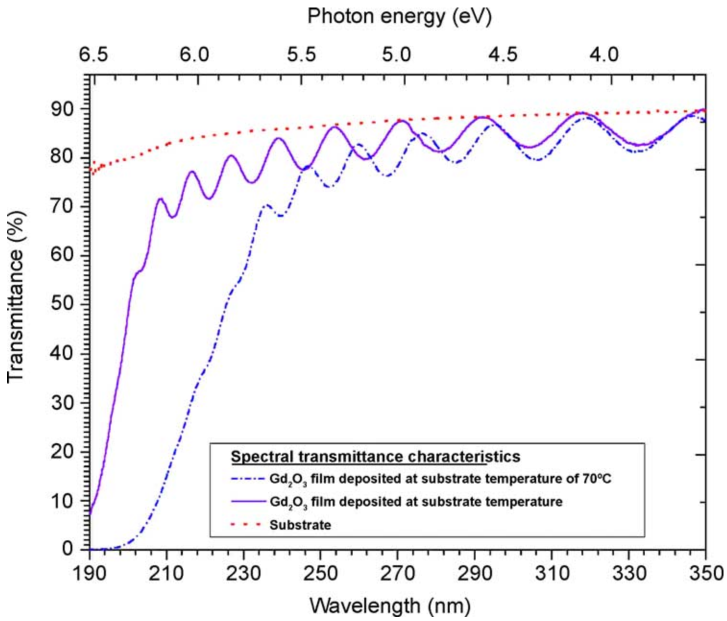

Fig. 1. Spectral transmittance of gadolinia films deposited at ambient and 70 °C temperature respectively. Influence of small amount of substrate temperature on the film's optical properties can be observed from this plot.

extinction coefficient and thickness of the thin films [9,10]. Besides, the band gaps have also been computed for all the films from the spectral transmittance data. It is very interesting to note that, most of the gadolinia films have its usable transmissions went below 190 nm, which qualitatively indicated band gap values should be greater than 6.52 eV. For such films, an appropriate numerical extrapolation method has been employed to compute the transmission value below 190 nm using the equation given below.

$$T(\lambda) = e^{(a+b/\lambda+c\ln(\lambda))} \quad (1)$$

where T and λ are the transmittance of the film and wavelength of the light respectively. And a, b, c are coefficients of extrapolating equation. The present band gap values have been computed from the absorption coefficient (α), which has been calculated from the extrapolated spectral transmission values [6]. In addition, optical constants and band gap values of a few gadolinia films have been computed from spectroscopic phase modulated ellipsometric measurements in order to have a comparative study on their values. For ellipsometric data analyses, a more realistic Tauc–Lorenrtz (TL) dispersion model has been employed to compute band gaps of these films [11]. It is interesting to note that the band gap values computed from extrapolated transmittance data from Eq. (1) have shown reasonably good agreement with the band gaps calculated from the ellipsometric measurements which justifies the use of Eq. (1) for the extrapolation.

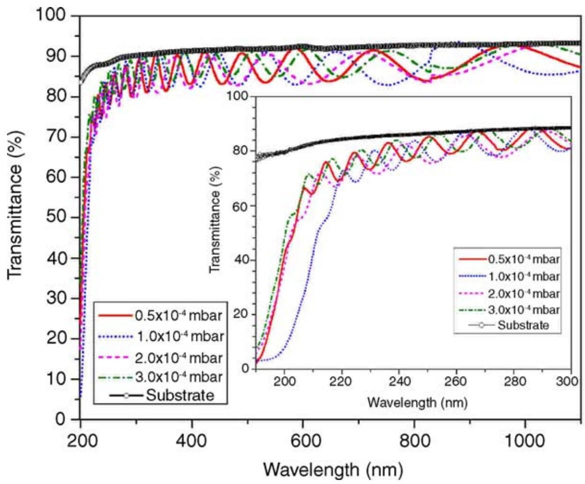

Fig. 2. Spectral transmittance of gadolinia films deposited at different oxygen pressures. The rate of evaporation is kept at 10 Å/s.

Table 1
Optical constants of gadolinia thin films extracted from spectral transmittance measurements

Deposition conditions			Refractive index (at λ = 600 nm)	Computed physical thickness (nm)
Oxygen pressure (10^{-4} mbar)	Rate of evaporation (Å/s)	Approximate optical thickness (at monitoring wavelength λ_m = 600 nm)		
0.5	10	~9λ/4	1.79	816.7
1	10	~9λ/4	1.82	772.9
1.5	10	~7λ/4	1.81	590.6
3	10	~9λ/4	1.76	861.1
1	5	~8λ/4	1.77	712.3
1	10	~9λ/4	1.82	772.94
1	15	~8λ/4	1.81	703.7
1	20	~9λ/4	1.8	731.5

In our present investigation, the deposition parameters such as rate and the oxygen pressure have been observed to affect the optical constant and band gap values largely. The detailed results of optical characterization have been presented in the Section 3.

2.2. Atomic force microscopy characterization

It is imperative that microroughness of the thin films has to be taken in to account for developing optical coatings especially in the UV region [12]. It is well known that optical coating technology moves to embrace shorter wavelength for manufacturing high-quality optical components for applications in ultraviolet regions especially for lithographic uses. Hence, the demand for high quality UV optical coatings has been rising constantly. In the case of optical surfaces, the root-mean-square (rms) roughness is normally used to characterize the surfaces. This parameter is not only related to the light scattering but also gives the user an idea about the quality of the surface under investigation.

In the present experiment, atomic force microscopy has been used to measure the surface topography and this information has been subsequently used to optimize the deposition parameter to get low scatter thin films [13]. AFM measurements have been performed with NT-MDT's Solver-P47H

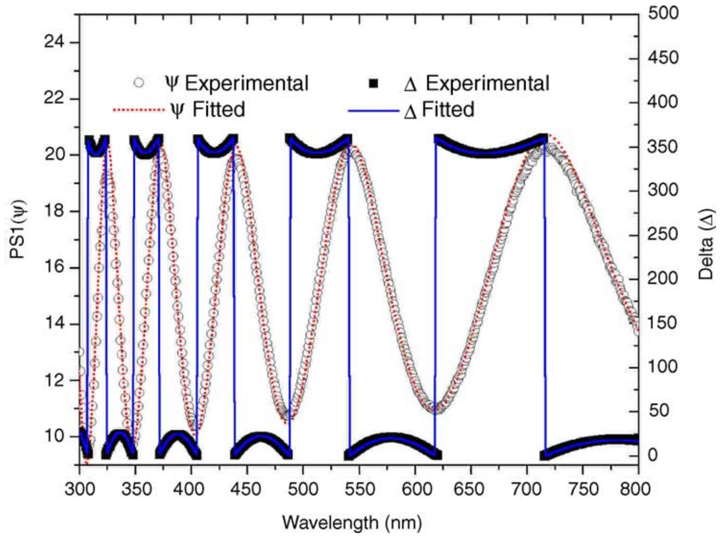

Fig. 3. Plots of measured and fitted ellipsometric parameters Ψ and Δ for gadolinia films deposited at the rate of 15 Å/s and the oxygen pressure of 1×10^{-4} mbar.

atomic force microscope. The contact mode operation has been employed for the measurements on the EB-deposited gadolinia films. AFM tip of Si_3N_4 having approximate values of radius of curvature of 10 nm, force constant of 0.6 N/m and the resonant frequency of 75 kHz has been used for the measurements. AFM measurements have been performed on all samples for the comparison studies with the scan area and step size of 5 μm × 5 μm and 19.53 nm, respectively. All the AFM measurement consists of 256 × 256 data points in the scanned image. The results of AFM characterization are presented in the following section.

3. Results and discussions

Rare earth gadolinia films have not only exhibited interesting optical properties but also opened up possibility of utilizing this material for making metal

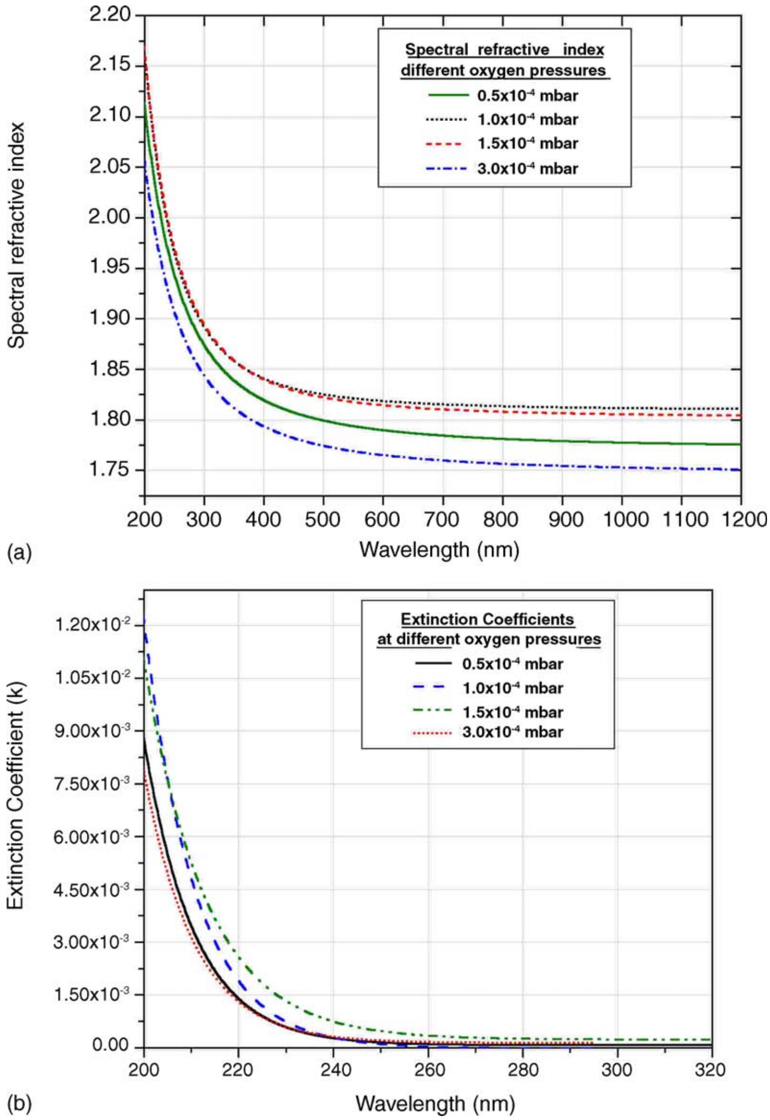

Fig. 4. (a) Spectral refractive index; (b) extinction coefficients of gadolinia films deposited on unheated quartz substrate at different oxygen pressures. The rate of evaporation is kept at 10 Å/s.

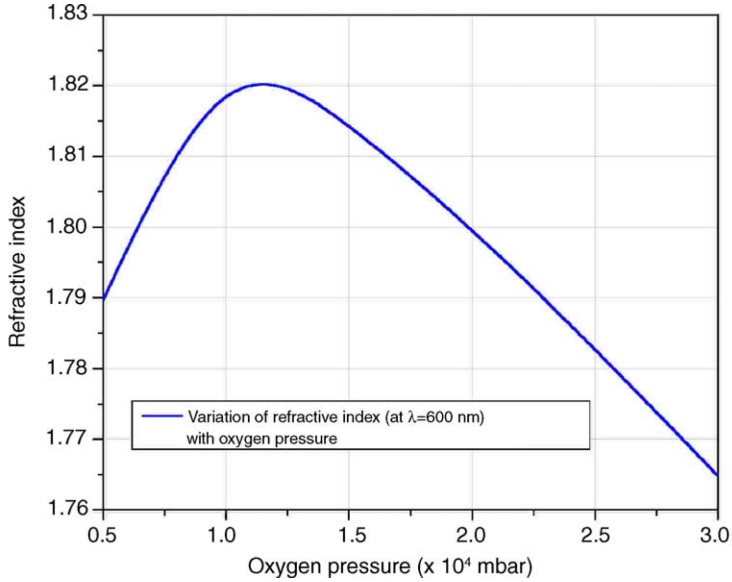

Fig. 5. Plot of variation of refractive index (at λ = 600 nm) of gadolinia films with oxygen pressure. During the deposition, substrate temperature and rate of evaporation were kept at ambient and 10 Å/s, respectively.

dielectric filters and coatings on temperature sensitive substrates. This film material has shown some amount of variations in optical properties with respect to substrate temperature like most other similar refractory oxides. The effect of a small amount of substrate temperature of 70 °C on the optical properties is depicted in Fig. 1. It can be seen from this figure that film deposited at ambient substrate temperature has shown some transmission even below 190 nm, where as film deposited at 70 °C substrate temperatures has depicted almost zero transmission even at 200 nm. It can therefore, be inferred that low ambient deposition improves the band gap value substantially. Besides, we also have some interesting observations while monitoring these films through quartz crystal monitor. While depositing these films, the saturation thickness of the quartz crystals depicted higher values (over 40% increase in the crystal health values) for these ambient temperature films in comparison to several other popular dielectric film materials like TiO_2, ZrO_2, etc. This aspect can be correlated to the good adhesion and low-stress factors of such films even at room temperature conditions. For several such reasons, we have carried out our systematic study on optical properties of gadolinium oxide films at ambient substrate temperature conditions. In the present study,

Table 2
Comparison of band gap values computed from ellipsometric measurements and spectrophotometric measurements

Deposition conditions		Bang gap (ellipsometry) (eV)	Bandgap (spectrophotometry) (eV)
Oxygen pressure (10^{-4} mbar)	Rate of evaporation (Å/s)		
0.5	10	6.643 ± 0.197	6.89
1	10	6.470 ± 0.240	6.82
1.5	10	6.974 ± 0.262	6.96
3	10	6.841 ± 0.239	7.02
1	5	6.633 ± 0.122	6.78
1	10	6.470 ± 0.240	6.82
1	15	6.875 ± 0.088	7.01
1	20	6.451 ± 0.195	6.71

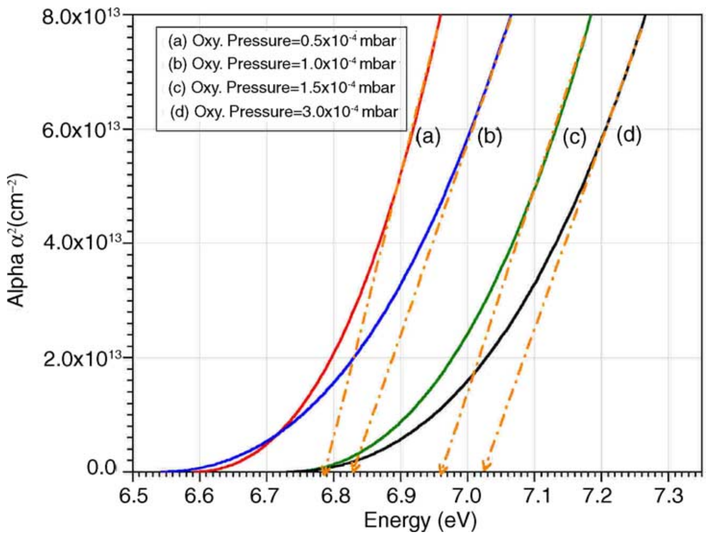

Fig. 6. Graphical determination of optical band gap of gadolinia films deposited on unheated quartz substrate under oxygen pressure of: (a) 0.5×10^{-4} mbar; (b) 1.0×10^{-4} mbar; (c) 1.5×10^{-4} mbar; (d) 3.0×10^{-4} mbar; respectively. The rate of evaporation is kept at 10 Å/s.

oxygen pressure and rate of evaporation have been observed to influence the optical, morphology and surface properties. However, the optimum optical property and surface topography of gadolinia films have been obtained by systematically varying the rate and oxygen pressure during the process.

3.1. Influence of oxygen pressure on optical properties

Investigation on the influence of oxygen pressure on optical properties is essential in designing and developing multilayer thin film optical devices. It is

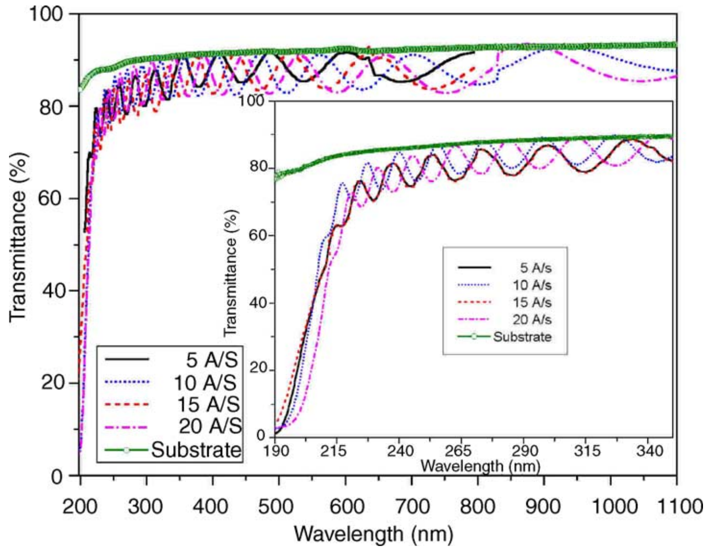

Fig. 7. Spectral transmittance of gadolinia films deposited at different evaporation rates. The substrate temperature and oxygen pressure were kept at ambient and 1.0×10^{-4} mbar, respectively.

well known that oxygen pressure changes the stoichiometry of the thin films, which eventually decides the optical constant of the thin films. In this present experiment, the oxygen pressure has been varied from 0.5×10^{-4} to 3×10^{-4} mbar and the rate of evaporation is kept at 10 ?/s. In addition, the substrate has been kept at ambient temperature conditions. The deposited thin films have been characterized for their spectral transmittances, which are portrayed in Fig. 2. Subsequently the envelope method has been employed to extract optical constant of the thin films [9,10]. Table 1 portrays the values of refractive index and the physical thickness of gadolinia films derived from this envelope method. In addition to spectrophotometric measurements, a phase modulated ellipsometric measurement techni-

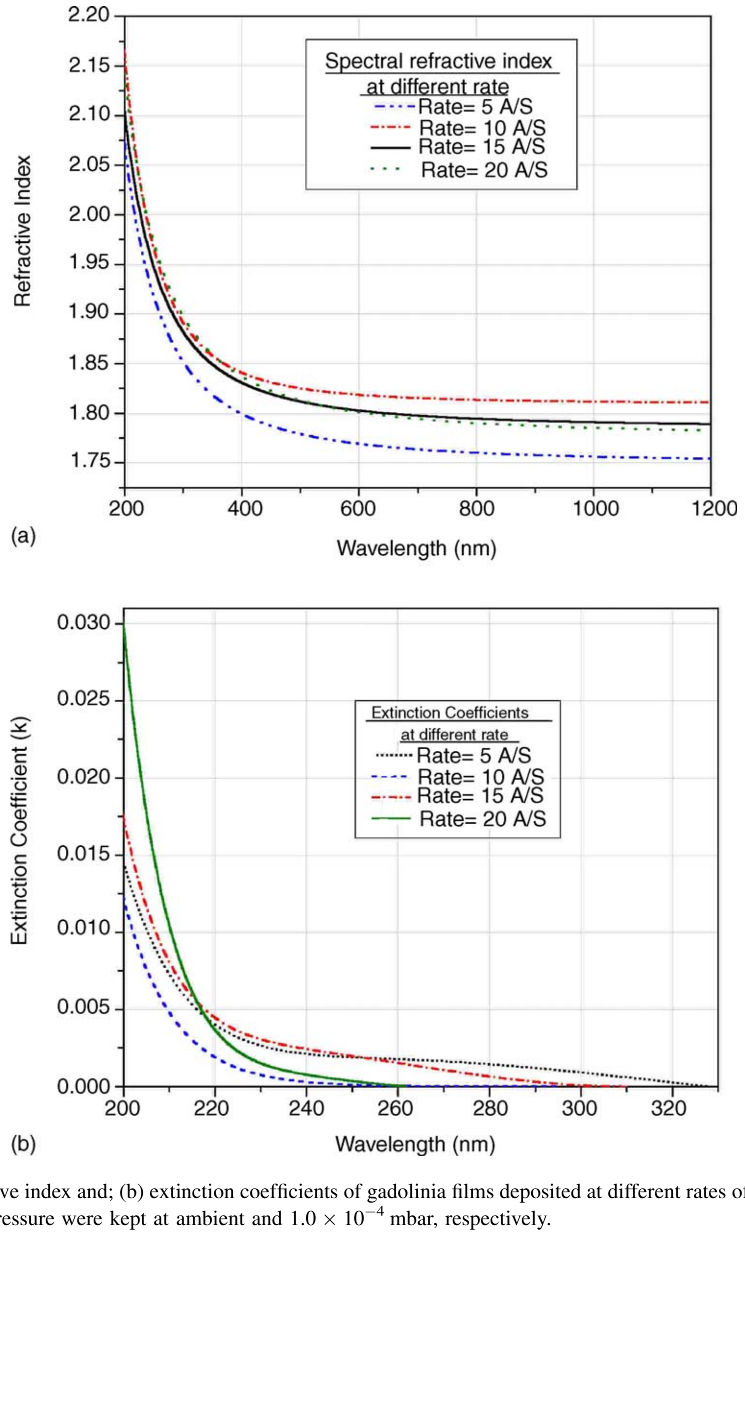

Fig. 8. (a) Spectral refractive index and; (b) extinction coefficients of gadolinia films deposited at different rates of evaporation. The substrate temperature and oxygen pressure were kept at ambient and 1.0×10^{-4} mbar, respectively.

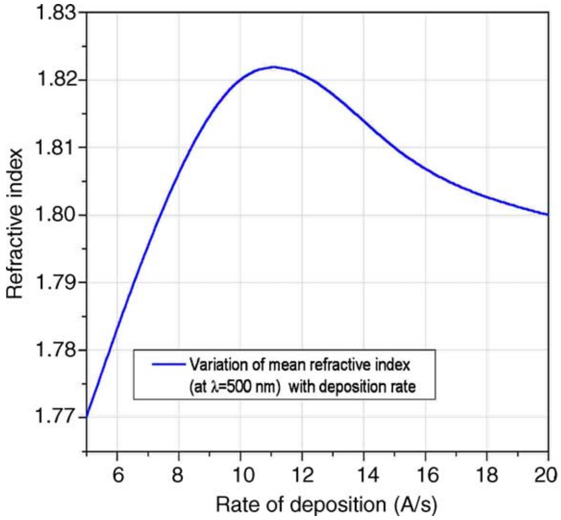

Fig. 9. Plot of variation of refractive index (at $\lambda = 600$ nm) of gadolinia films with rate of evaporation. The substrate temperature and oxygen pressure were kept at ambient and 1.0×10^{-4} mbar, respectively.

que has also been adopted to verify some of the optical properties of a few samples. The variation of experimental ellipsometric parameters Ψ and Δ and the corresponding fitted curves using Tauc–Lorenrtz model have been portrayed in Fig. 3 for a typical gadolinia sample film.

Fig. 4a and b depict the computed spectral refractive index and extinction coefficient of the thin films deposited at various oxygen partial pressures. It can be seen from this figure that there is a conspicuous change in spectral refractive index with respect to the oxygen pressure indicating its strong influence on optical properties. In order to understand the systematic trend due to the oxygen pressure, the refractive index values of these films at the wavelength 600 nm is plotted with respect to this parameter (as shown in Fig. 5). It has been seen from Fig. 5 that at optimum oxygen pressure of 1×10^{-4} mbar, gadolinia films yielded highest refractive index. During our current investigation, the band gaps of these films have primarily been computed from the spectrophotometric measurements using the Eq. (1). Besides, as a representative study, band gap values of a few gadolinia films have also been determined from ellipsometric measurements using Tauc–Lorenrtz model. The band gap values computed using these methods have been compared in Table 2. It can be seen from the table that both the measurements have almost predicted similar band gap values within their respective experimental deviations. Fig. 6 depicts the band gap of the gadolinia films deposited at different oxygen pressure. It can be seen from this figure that, gadolinia films grown at oxygen pressure of 3×10^{-4} mbar and ambient substrate temperature

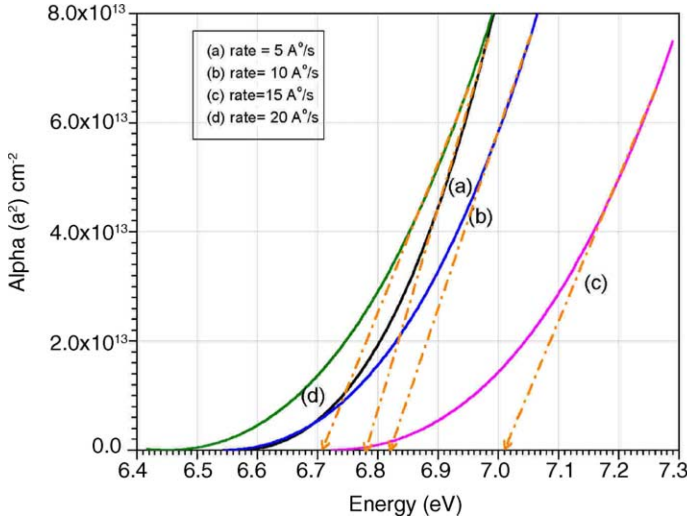

Fig. 10. Graphical determination of optical band gap of gadolinia films deposited on unheated quartz substrate at the rates of deposition of: (a) 5 Å/s; (b) 10 Å/s; (c) 15 Å/s; (d) 20 Å/s, respectively. The oxygen pressure is kept at 1×10^{-4} mbar.

have shown higher band gap value of close to 7 eV. Such a value is higher than the band gap values of the high temperature sample films reported earlier [7]. At this oxygen pressure, the refractive index of such a film is relatively small as expected from the theory of thin film band gaps. Such a high band gap in this film can be attributed to the integrated effects of the process parameters adopted in the present reactive EB deposition process. It is important to note that the films deposited at optimum oxygen pressure of 1×10^{-4} mbar have shown lower band gap value; on the other hand, they have shown predictably higher refractive indices.

3.2. Influence of rate of deposition on optical properties

Rate of deposition is another important process parameter, which also influences the optical properties of the thin films through the nucleation growth stages. Its effect also needs careful study before deciding appropriate parametric conditions to develop multilayer devices. In this present experiment, the rate of deposition has been varied from 5 to 20 Å/s, while the oxygen pressure and the substrate temperature are kept at 1×10^{-4} mbar and ambient temperature conditions respectively. Films deposited at various rate of deposition have been characterized for the optical properties from the spectral transmittance measurements, which are portrayed in Fig. 7. Fig. 8a and b portrays computed spectral refractive index and extinction co-efficient of the films deposited at different rate of depositions. It is clear from this figure that rate also influences the refractive index largely. Film deposited at the optimum rate of 10 Å/s has shown highest refractive index. The systematic variation of refractive index with rate can be observed from Fig. 9. In this figure, the refractive index is plotted at the wavelength of 600 nm. In this figure a rapid increase in the refractive index value can be

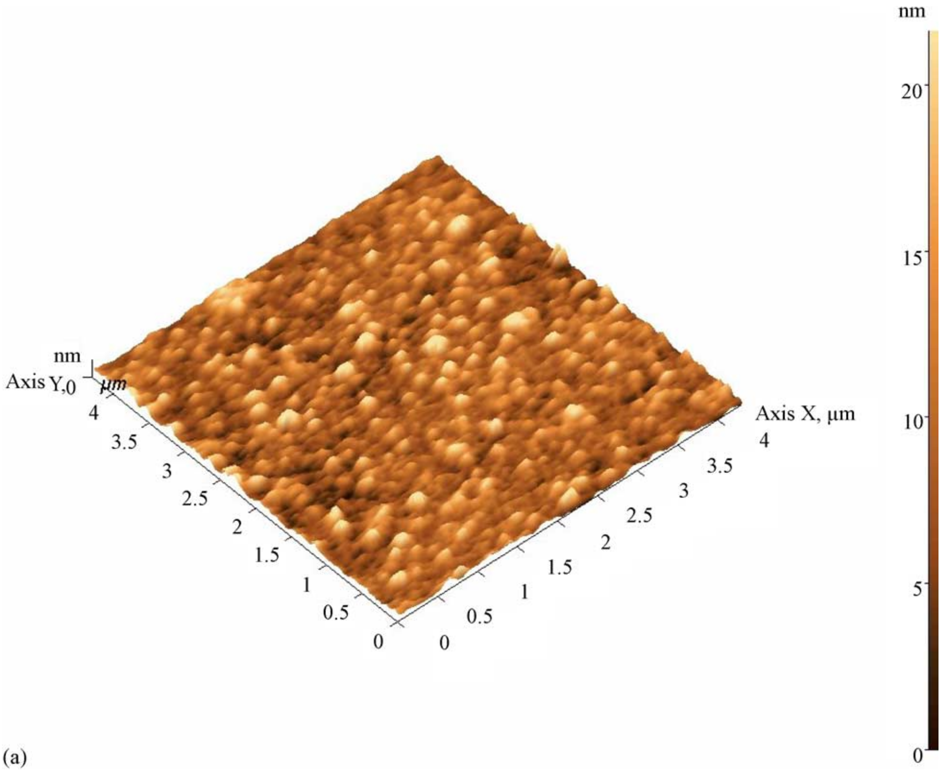

Fig. 11. AFM surface topographic image of gadolinia films deposited on quartz substrate at the oxygen pressure and the rate of deposition of: (a) 1×10^{-4} mbar, 20 Å/s; (b) 1×10^{-4} mbar, 10 Å/s; and (b) 3×10^{-4} mbar and 10 Å/s, respectively.

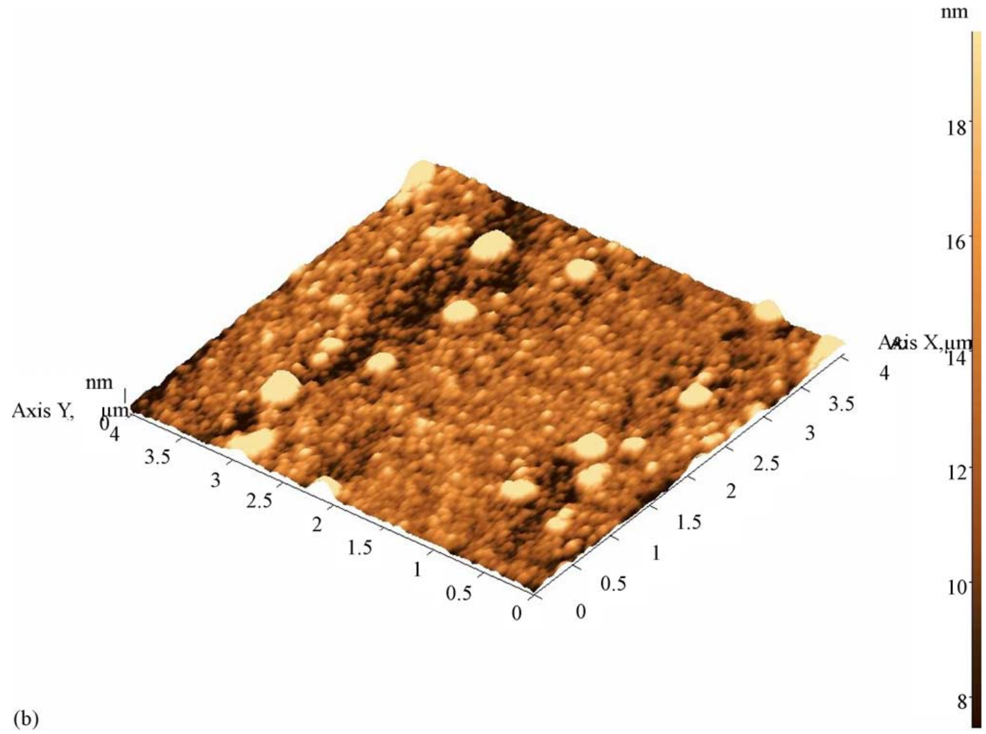

Fig. 11. (*Continued*).

observed as the rate is increased up to the optimum value of 10 Å/s, however slow decrease in the refractive index value as the rate is increased further. This suggests that effect of rate of evaporation on optical properties of gadolinia films is not as dominant as the effect of oxygen pressure. Fig. 10 portrays optical band gap of gadolinia films deposited at different rates of deposition. It can be seen from this figure that the rate of deposition also has strong influence on the band gap of the gadolinia films. The higher value of band gap (~7 eV) has been obtained for the films deposited at the rate of 15 Å/s.

3.3. *Surface characterization using AFM*

As mentioned in the earlier section that surface properties are imperative for optical coatings in UV application. Fig. 11 shows the surface morphology of gadolinia films deposited at three different deposition conditions. It can be inferred from these figures that films with good morphology can be even obtained at ambient substrate temperature conditions. Fig. 11a and c depict the topography of the film deposited at two extreme deposition conditions, which are high rate of 20 Å/s (oxygen pressure = 1×10^{-4} mbar) and high oxygen pressure of 3×10^{-4} mbar (rate = 10 Å/s). However, Fig. 11b depicts the topography of the film deposited at the optimum conditions, i.e., the rate and oxygen pressure value of 10 Å/s and 1×10^{-4} mbar, respectively. It can be seen from Fig. 11 that film deposited at optimum rate of 10 Å/s and oxygen pressure of 1×10^{-4} mbar has shown smooth topography depicting very small grain structure on its surface. In order to study the effect of oxygen pressure and rate of deposition on the surface properties systematically, AFM measurements have been performed on all samples with the scan area of 5 μm × 5 μm. The plot of RMS surface roughness values computed for the gadolinia samples deposited at different oxygen pressure is portrayed in Fig. 12. It can be seen from this figure that variation in the oxygen pressure alters the surface roughness values to a great extent. Furthermore, the optimum pressure of

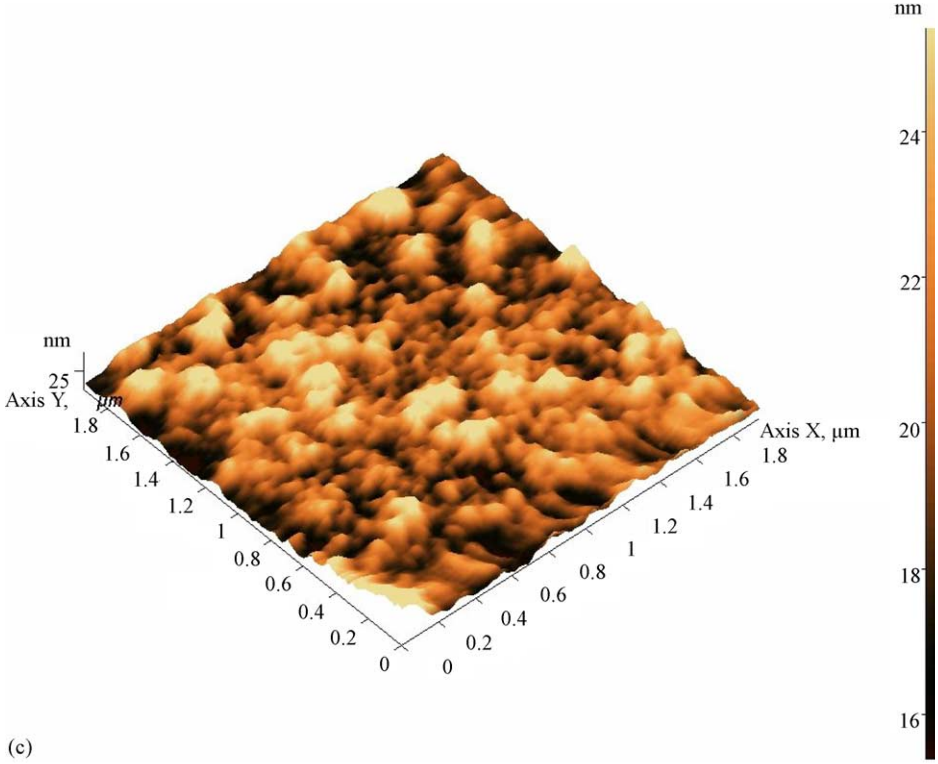

Fig. 11. (*Continued*).

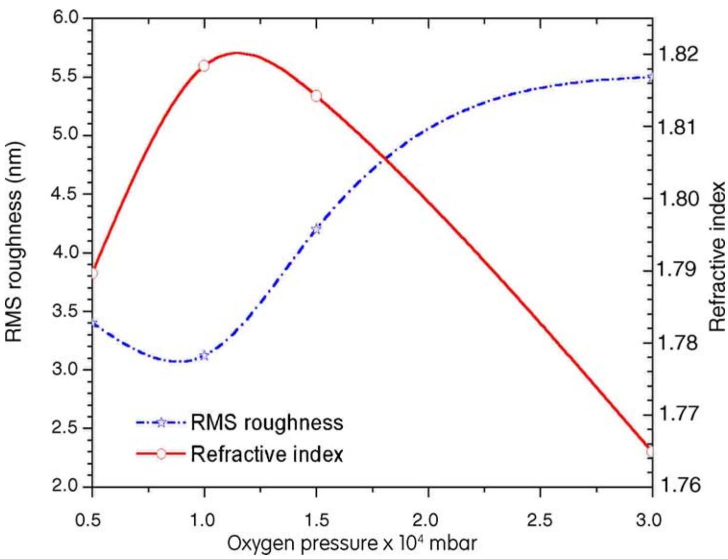

Fig. 12. Variation of microroughness and refractive index of gadolinia films deposited at different oxygen pressures. The rate of deposition is kept at 10 Å/s during the deposition. The scan area used for AFM measurement is 5 μm × 5 μm.

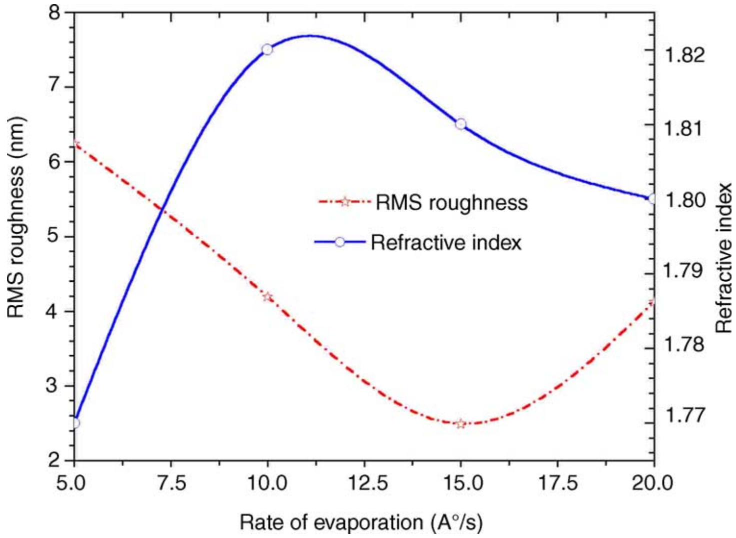

Fig. 13. Variation of microroughness and refractive index of gadolinia films deposited at different rates of deposition. The oxygen pressure is kept at 1×10^{-4} mbar during the deposition. The scan area used for this measurement is 5 μm × 5 μm.

1×10^{-4} mbar yielded low surface roughness value (RMS roughness 3.12 nm). It can also be noted from the same figure that this value oxygen pressure has yielded the highest refractive index. However, the extreme values of oxygen pressures have yielded high surface roughness values.

Fig. 13 portrays plot of variation of RMS roughness values of samples prepared at different rate of depositions. It can be seen from this figure that low surface roughness value has been obtained for the sample prepared at the optimum rate of 15 Å/s. Besides, the roughness variation follows an opposite trend when it is compared with the rate dependent refractive index variation. Therefore, it can be inferred that the rates of deposition and oxygen pressures have strong influences on optical properties of gadolinia films when the substrate is maintained at the ambient temperature condition. The optical and surface properties also noticed to be highly correlated with each other.

4. Conclusions

Gadolinia films have been grown on quartz substrate using reactive electron beam evaporation techniques at ambient substrate temperature. The oxygen pressure and rate of evaporation have been systematically varied during the deposition. Spectrophotometric, ellipsometric and AFM measurements have been carried out in order to study the optical and surface properties of the gadolinia samples. AFM measurements revealed that gadolinia films with superior morphologies could even be obtained even at ambient substrate temperature conditions. This observation is a valuable addition to the previous observations made on this oxide material as well as other rare earth oxide materials. By varying the rate and oxygen pressure, optimum optical and surface properties (morphologies) in the gadolinia films have been obtained. Besides, band gap value in such films of as high as 7.02 eV has been achieved. It has been observed from our investigation that the rates of deposition and oxygen partial pressures have strong influence on optical and topographies of gadolinium oxide thin films. In addition, optical and morphological properties have shown good correlation with each other.

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References

[1] E. Ritter, Phys. Thin films, Academic Press, New York, 1975, pp. 1–49.
[2] R. Chow, S. Falabella, G.E. Loomis, F. Rainer, C.J. Stolz, M.R. Kozlowski, Appl. Opt. 32 (1993) 5567.
[3] T. Marcinow, K. Truszkowska, Appl. Opt. 20 (1981) 1755.
[4] A.A. Dakhel, J. Opt. A: Pure Appl. Opt. 3 (2001) 452.
[5] T. Wiktorczyk, Thin Solid Films 405 (2002) 238.
[6] N.K. Sahoo, S. Thakur, M. Senthilkumar, D. Bhattacharyya, N.C. Das, Thin Solid Films 440 (2003) 155.
[7] N.K. Sahoo, M. Senthilkumar, S. Thakur, D. Bhattacharyya, Appl. Surf. Sci. 200 (2002) 219.
[8] N.K. Sahoo, S. Thakur, M. Senthilkumar, N.C. Das, Appl. Surf. Sci. 214 (2003) 259.
[9] R. Swanepoel, J. Phys. E: Sci. Instrum. 16 (1983) 1214.
[10] R. Swanepoel, J. Phys. E: Sci. Instrum. 17 (1984) 896.
[11] G.E. Jellison Jr., F.A. Modine, Appl. Phys. Lett. 69 (1996) 371.
[12] A. Duparre, Light scattering of thin dielectric films, in: Hand Book of Optical Properties, vol. 1, CRC Press, 1995.
[13] G. Binnig, C.F. Quate, Ch. Gerber, Phys. Rev. Lett. 56 (1986) 930.