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Optical properties and morphological changes in gadolinia films deposited under ambient substrate temperature conditions

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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 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 spectroscopic phase modulated ellipsometric and spectrophotometric 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; Phase modulated spectroscopic ellipsometry

1. Introduction

Thin film refractive 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, ultraviolet (UV) and deep UV spectral regions. In most optical coating applications, reactive electron beam (EB) evaporation technique has been preferentially as well as successfully adopted for depositing oxide thin films and multilayers. In such deposition process, high quality dense and stable oxide thin films are most commonly obtained only when substrates are maintained at elevated temperatures [1]. Nevertheless, ambient substrate temperature deposition condition is of great importance due to their varieties of requirements such as development of metal-dielectric filters and application-specific coatings on temperature sensitive substrates etc. In this article, we have 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 reasonably good transmission down to 250 nm [2–4]. They also have interesting physical properties relating to various optical coating

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applications [5]. In addition, these are characterized by a good chemical, thermal and mechanical stability when used under multilayer environments [5]. Gadolinia (Gd_2O_3) is one of the rare earth oxides, which has the potential to be used in deep UV applications. In earlier studies on gadolinia films, optical properties have been reported on films mostly deposited on quartz substrate at elevated substrate temperatures [6–8]. However, in our present study, gadolinia films 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 on heated substrates. In this work, 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 spectrophotometry, phase modulated ellipsometry and atomic force microscopy (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 the starting material. A water-cooled 8 KW electron beam gun of M/s VTD make 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 (i.e., without any heating). 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 our experiments, the rate of deposition has been varied from 5 Å/s to 20 Å/s, where as, the oxygen pressure has been varied from 0.5×10^{-4} mbar to 3×10^{-4} mbar. All the films have been deposited with the optical thickness in the range of $7\lambda/4$–$9\lambda/4$ ($\lambda/4$ 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 method of characterization and their results have been presented in the following sections.

2.1. Optical characterization

Optical characterization of gadolinium oxide films has been carried out from spectral transmittance measurements, which were obtained through Shimadzu UV3101PC spectrophotometer system. These measurements have been performed in the wavelength region from 190 nm to 1500 nm. The envelope method has been employed to extract refractive index, 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 even shown transmitting well below 190 nm, which qualitatively indicated band gap values greater than 6.52 eV. For such films, an appropriate numerical extrapolation method has been employed to compute the transmission spectra below 190 nm using the equation given below.

$$T(\lambda) = \mathrm{e}^{\left(a+\frac{b}{\lambda}+c\ln(\lambda)\right)} \tag{1}$$

where, T and λ are the transmittance of the film and wavelength of the light respectively, and a, b, c are the coefficients of extrapolating equation. The present band gap values have been computed from the absorption coefficient (α), using 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 of the film properties using two different techniques. The ellipsometric measurements have been carried out in the spectral region of 300–800 nm. A more realistic Tauc–Lorenrtz (TL) dispersion model has been employed to compute dispersive refractive index, extinction coefficient and band gap 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 measurement which justifies the use of Eq. (1) for the extrapolation.

In this investigation, the deposition parameters such as rate and the oxygen pressure have been observed to affect the optical constant and band gap values to a great extent. The detailed experimental results of the optical characterization have been presented in 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 and deep-UV optical coatings has been rising constantly. In such case of the precision optical thin films, 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 (AFM) has been used to measure the surface topography and this information has been subsequently used to optimize the deposition parameter to achieve low scatter thin films [13]. AFM measurements have been performed with NT-MDTs Solver-P47H 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 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 over a scan area and step size of $5\,\mu m \times 5\,\mu m$ and 19.53 nm respectively. All the AFM measurement consists of 256×256 data points in the scanned image. The results of this AFM characterization are presented in Section 3.

3. Results and discussion

Rare earth gadolinia films have not only exhibited interesting optical properties but also opened up possibility of utilizing this material for making metal dielectric filters and coatings on temperature-sensitive substrates. This film material has depicted some 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 presented in Fig. 1. It can be seen from this figure that film deposited at ambient substrate temperature has shown some weak transmission even below 190 nm, where as film deposited at 70 °C substrate temperatures has displayed 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 using quartz crystal monitor. While depositing these

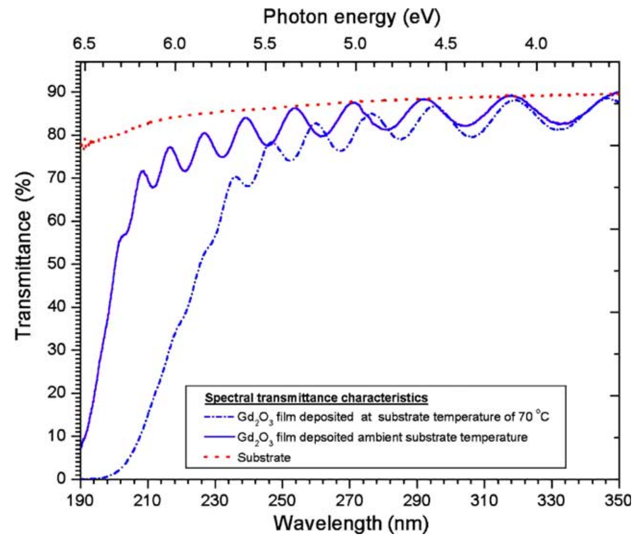

Fig. 1. Spectral transmittance of gadolinia films deposited at ambient and 70 °C temperature respectively. Influence of small amount of substrate temperature on the film's optical properties can be observed from this plot.

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 attributed 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, 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 achieved 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 well known that oxygen pressure changes the stoichiometry as well as void structures of the thin films, which eventually decides the optical constant of the films. In the present experiment, the oxygen pressure has been varied from 0.5×10^{-4} mbar to 3×10^{-4} mbar while maintaining the rate of evaporation at 10 Å/s and the substrate temperature at ambient conditions. The deposited films have been characterized for their spectral transmittances using the Shimadzu UV3101PC spectrophotometric system. Subsequently an envelope method has been employed to extract the optical constants of these thin films [9,10]. Besides, a phase modulated spectroscopic ellipsometric measurement technique has also been adopted to verify some of the optical properties of a few samples. Fig. 2 depicts typical ellipsometric measurements and modeling of gadolinia films deposited at the rate of 15 Å/s and the oxygen pressure of 1×10^{-4} mbar. The refractive index, extinction coefficients, thickness and band gap values of gadolinia films have also been determined from the ellipsometric data using a three layer modeling technique [7].

Fig. 3 shows the computed spectral refractive index (from spectrophotometric measurements) 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. In order to investigate the systematic trend, the spectral refractive values of these films at the wavelength 600 nm are plotted with respect to oxygen pressure (as shown in Fig. 4). It has been seen from this Fig. 4 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 been computed from the spectrophotometric as well as from the ellipsometric measurements. Fig. 5 depicts the band gap of the gadolinia films deposited at different oxygen pressures as computed from the spectrophotometric values. It can be seen from this figure that, gadolinia films grown at oxygen

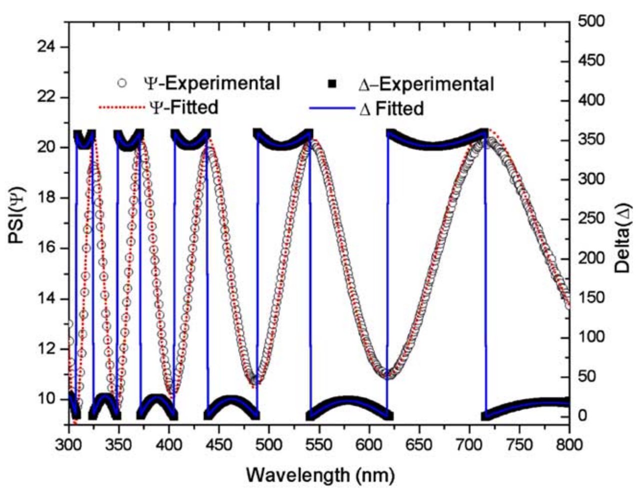

Fig. 2. The plots of measured and fitted ellipsometric parameters Ψ and Δ for gadolinia films deposited at the rate of 15 Å/s and the oxygen pressure of 1×10^{-4} mbar.

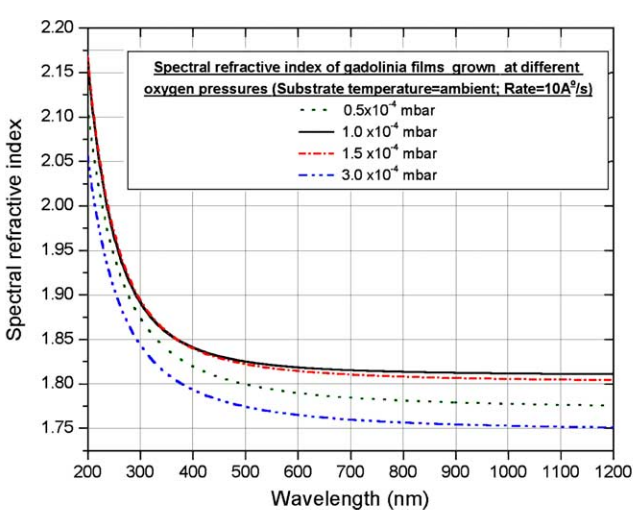

Fig. 3. Spectral refractive index of gadolinia films deposited on unheated quartz substrate at different oxygen pressures. The rate of evaporation is kept at 10 Å/s.

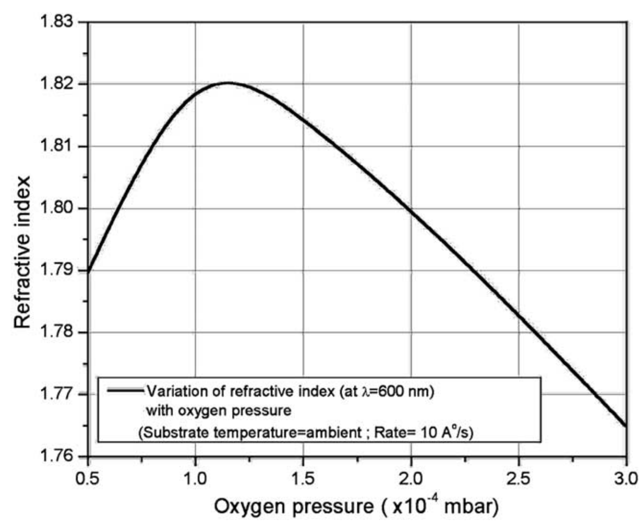

Fig. 4. Plot of variation of refractive index (at $\lambda = 600$ nm) of gadolinia films with oxygen pressure. During the deposition, substrate temperature and rate of evaporation were kept at ambient and 10 Å/s respectively.

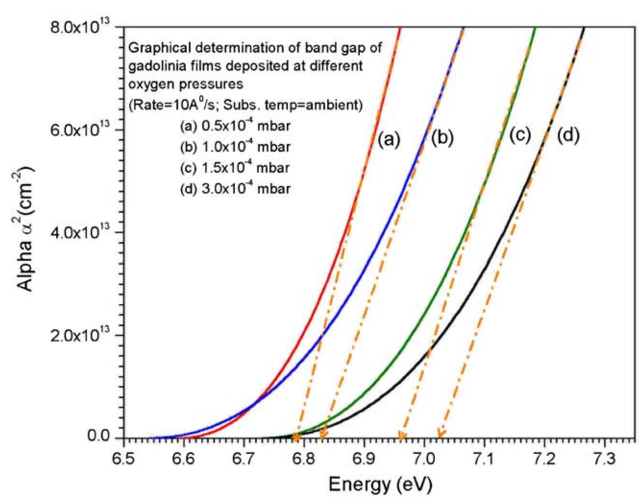

Fig. 5. Graphical determination of optical band gap of gadolinia films deposited on unheated quartz substrate under oxygen pressure of (a) 0.5×10^{-4} mbar; (b) 1.0×10^{-4} mbar; (c) 1.5×10^{-4} mbar; (d) 3.0×10^{-4} mbar respectively. The rate of evaporation is kept at 10 Å/s.

pressure of 3×10^{-4} mbar have shown higher band gap value close to 7 eV, which is appreciably higher than the band gap values reported earlier [7]. At this oxygen pressure, the refractive index of such a film also shows a lower value 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. Such values are well supported by the ellipsometry. Table 1 provides a comparison of band gap values computed from the both measurements. It can be observed from the table that both the measurements predict almost similar band gap values. This aspect justifies the use of extrapolation Eq. (1) for the band gap calculation from the spectrophotometric measurements.

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 at growth stages. Its effect also needs careful study before deciding appropriate parametric conditions to develop precision multilayer devices. In the present experiment, the rate of deposition has been varied from 5 Å/s to 20 Å/s, while maintaining the oxygen pressure and the substrate temperature at 1×10^{-4} mbar and ambient temperature conditions respectively. Films deposited at various rates of deposition have been characterized for the optical properties from the spectral transmittance as well as ellipsometric measurements. Fig. 6 portrays computed spectral refractive index of the films deposited at different rate of depositions using spectrophotometric technique. It is clear from this figure that rate also influences the refractive index appreciably. Film deposited at the optimum rate of 10 Å/s has shown highest refractive index. Spectral refractive index of gadolinia films have also been computed from the phase modulated spectroscopic ellipsometric measurements. Fig. 7 depicts refractive index of the above gadolinia films using ellipsometric data analysis. One can see a close match in the refractive index values obtained using two different measurement and analysis techniques.

The systematic variation of refractive index value at the wavelength of 600 nm with rate can be easily observed from Fig. 8 signifying the parametric dependence. An appreciable change in the refractive index value can

Table 1
Comparison of band gap values computed from ellipsometric measurements and spectrophotometric measurements

Deposition conditions		Bang gap (eV) (ellipsometry)	Band gap (eV) (spectrophotometry)
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

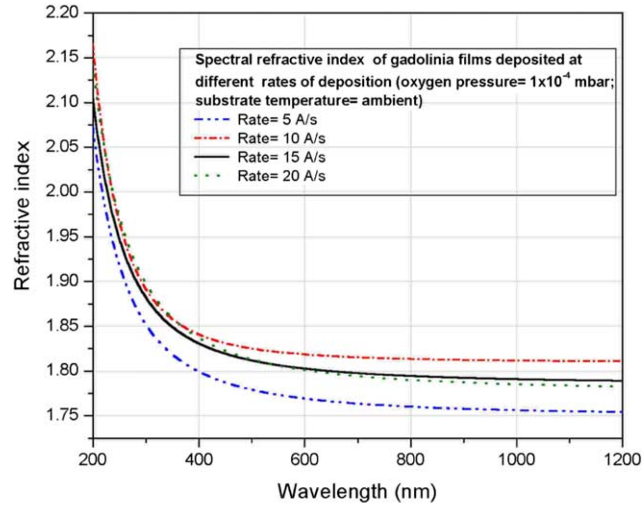

Fig. 6. Spectral refractive index of gadolinia films deposited at different rates of evaporation. The oxygen pressure is kept at 1×10^{-4} mbar.

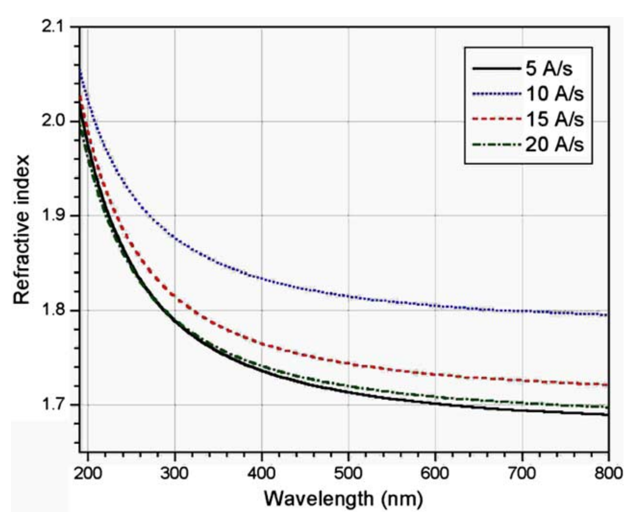

Fig. 7. Spectral refractive index of gadolinia films deposited at different rates of evaporation (computed from ellipsometric modeling). The oxygen pressure is kept at 1×10^{-4} mbar.

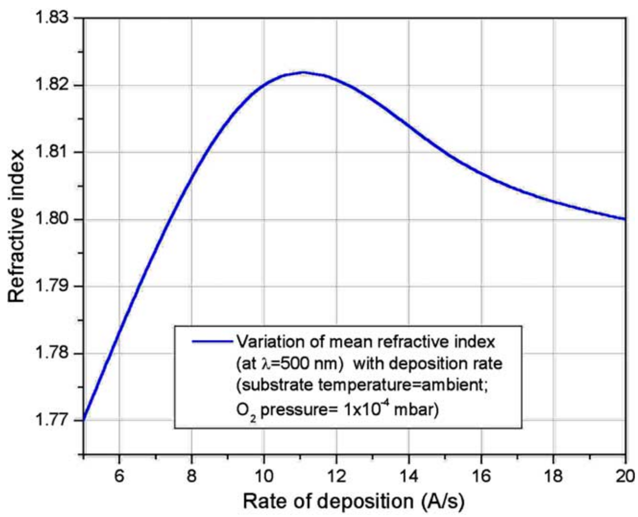

Fig. 8. Plot of variation of refractive index (at $\lambda = 600\,\text{nm}$) of gadolinia films with rate of evaporation. The substrate temperature and oxygen pressure were kept at ambient and 1.0×10^{-4} mbar.

be easily observed in this plot as the rate approaches an optimum value of 10 Å/s. Subsequently a slow decrease in the refractive index value can be noticed as the rate is increased further. The experimental data gathered by varying these process parameters suggest that increasing the oxygen pressure above 1×10^{-4} mbar (optimum value) reduces the refractive index appreciably, however increasing the evaporation rate above 10 Å/s (optimum value) does not reduce the index very much.

Fig. 9 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

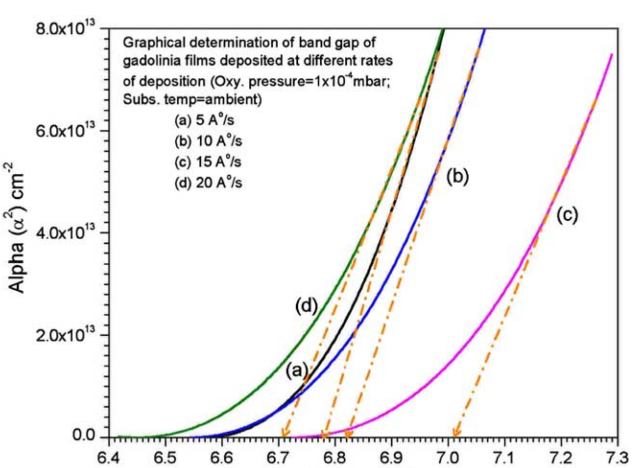

Fig. 9. Graphical determination of optical band gap of gadolinia films deposited on unheated quartz substrate at the rates of deposition of (a) 5 Å/s; (b) 10 Å/s; (c) 15 Å/s; (d) 20 Å/s respectively. The oxygen pressure is kept at 1×10^{-4} mbar.

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. Surface properties of gadolinia films have been measured using a NT-MDTs Solver P47H atomic force microscope. Fig. 10 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 as well. Fig. 10a and b depict the topographies of the films deposited at two extreme deposition conditions, one with high rate of 20 Å/s (optimum oxygen pressure of 1×10^{-4} mbar) and the other with high oxygen pressure of 3×10^{-4} mbar (optimum rate of 10 Å/s). However, Fig. 10c 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 observed from this figure 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 surface grain structure. 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 $5\,\mu\text{m} \times 5\,\mu\text{m}$. The plot of RMS surface roughness values computed for the gadolinia samples deposited at different oxygen pressures is portrayed in Fig. 11. It can be seen from this figure that variation in the oxygen pressure alters the surface roughness values. Furthermore, the optimum pressure of 1×10^{-4} mbar yielded low surface roughness value (RMS roughness 3.12 nm). It can also be noted from this figure that roughness and refractive index have opposite trends with respect to the oxygen pressure. Fig. 12 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 refractive index with the rate variation. From the above observation, it is clear that a higher value of the refractive index is always associated with a good topography. This is possibly due to a strong correlation amongst the refractive index, density factor and optimum grain sizes in the films under various parametric conditions.

Therefore, it can be inferred that the rates of deposition and oxygen pressures have strong influences on the optical and morphological properties of gadolinia films deposited under ambient temperature condition. The

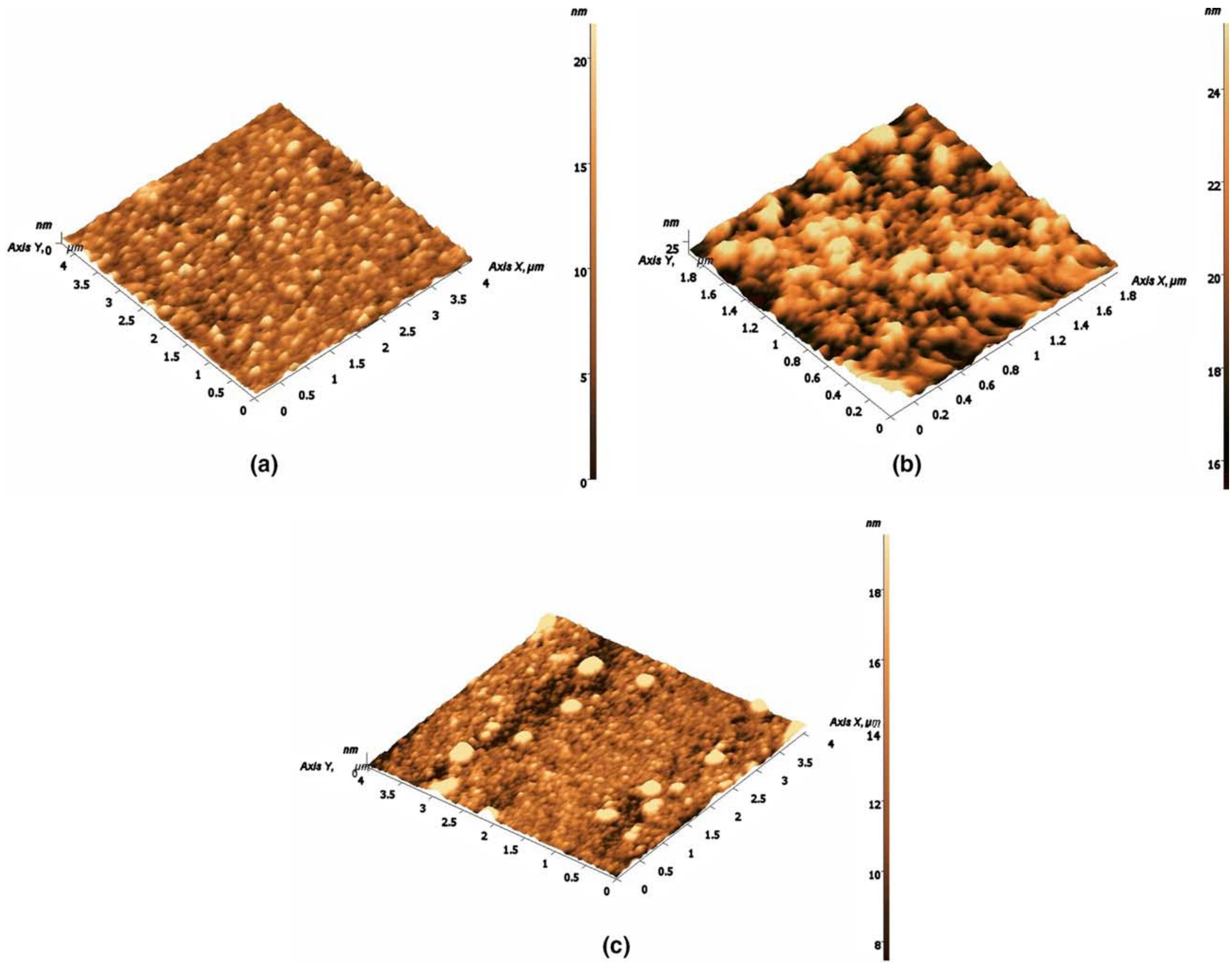

Fig. 10. AFM surface topographic image of gadolinia films deposited on quartz substrate at the oxygen pressure and the rate of deposition of (a) 1×10^{-4} mbar, 20 Å/s; (b) 3×10^{-4} mbar, 10 Å/s; and (c) 1×10^{-4} mbar, 10 Å/s respectively.

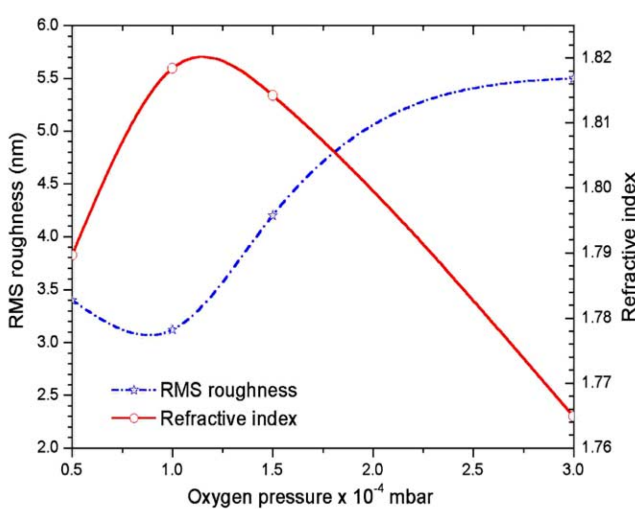

Fig. 11. Variation of microroughness and refractive index of gadolinia films deposited at different oxygen pressures. The rate of deposition is kept at 10 Å/s during the deposition. The scan area used for AFM measurement is $5\,\mu m \times 5\,\mu m$.

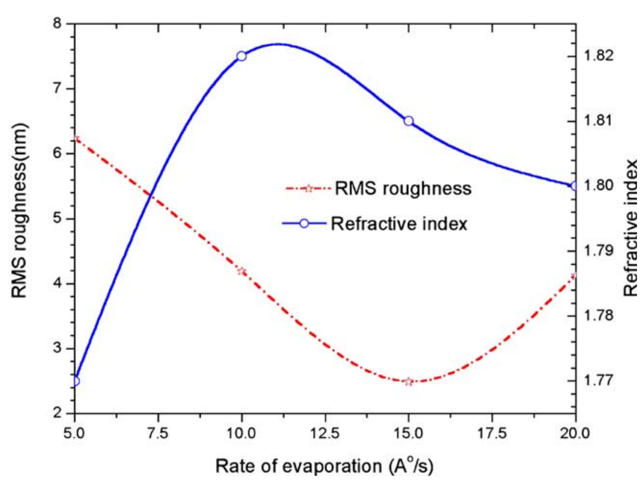

Fig. 12. Variation of microroughness and refractive index of gadolinia films deposited at different rates of deposition. The oxygen pressure is kept at 1×10^{-4} mbar during the deposition. The scan area used for this measurement is $5\,\mu m \times 5\,\mu m$.

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, phase modulated spectroscopic ellipsometric and AFM measurements have been carried out in order to study the optical and surface properties of the thin film gadolinia samples. AFM measurements revealed that gadolinia films with superior morphologies could even be obtained even at ambient substrate temperature conditions as well. This observation is a valuable addition to the various other previous observations made on this oxide material. 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 topographic properties of these thin films. In addition, optical and morphological properties have shown good correlation with each other.

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