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Correlation of optical and microstructural properties of Gd_2O_3 thin films through phase-modulated ellipsometry and multi-mode atomic force microscopy

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Abstract

Gadolinium oxide thin films have been prepared by electron beam evaporation with different reactive oxygen pressures at low ambient substrate temperature. These thin films have been analyzed with phase-modulated spectroscopic ellipsometry and multi-mode atomic force microscopy (AFM). The distinct influences of oxygen pressure on surface topographies, microstructures and refractive indices of the thin films have been observed from the results of these advanced measurements. Both these techniques have displayed very strong co-relationships in the characterisation results acquired through respective modes of measurements and data analysis. Unequivocally, these two techniques indicated an optimum value of the oxygen pressure leading to best optical and structural properties of such a novel optical coating material.

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Keywords: Gadolinium oxide; Microstructural properties; Optical properties; Ellipsometry; Surface topography; E-beam evaporation

1. Introduction

Optical coatings and multi-layer devices are established to be the most essential components in lasers, spectroscopy, optical communication and space applications [1]. Most of these applications demand precision optical coatings that are to be spectrally acceptable, mechanically stable, resistance to environmental influences and free from internal stress and defects. The improvement in material properties, deposition processes and the characterisation techniques are the prime routes to achieve such stable and complex optical coatings. Therefore, advanced deposition processes as well as novel material characterisations are gaining importance for achieving improved performances and reliabilities in optical coatings. With respect to characterisation of precision thin films, interfaces and multi-layers, both ellipsometry and atomic force microscopy (AFM) have received special attentions of thin film researchers and technologists. Both these techniques have their own merits and limits in thin film characterisations. For example, although AFM probes length scales much shorter than the nanometer [2]; it cannot measure the degree of correlation between the interfaces, where as ellipsometry provides much more detailed information in

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the bulk as well as interfaces besides deriving most of the optical properties of the sample film [3]. Similarly topographic and compositional fluctuations on the surface are easily detectable using AFM, where as ellipsometry conveniently probes such fluctuations well deep inside the film by appropriate multi-parametric modelling.

Phase-modulated spectroscopic ellipsometry adopts a very different approach with respect to conventional null-ellipsometry by incorporating a birefringence modulator to modulate the polarisation of the probing light beam at a high, well-defined frequency in characterising the thin films, interfaces and multi-layers more efficiently [4–6]. Such a technique provides the ellipsometers to have virtually no insensitive regions, low signal noise, and less influenced by small changes in the angle of incidence. The technique allows a fast response time and has a superior signal-to-noise ratio due to the use of lock-in detection and a high signal throughput. Also rapid data acquisition processes due to the phase modulations have facilitated the multi-angle and multi-wavelength measurements more efficiently especially for real time investigations. Therefore, in applications such as dynamic structural studies, compositional measurements and ellipsometric imaging, phase-modulated has significant advantages over conventional ellipsometric techniques.

Similarly over the years AFM techniques have been diversified with the integration of several additional modes of measurements and analyses for better precision, data acquisition and interpretation. Scanning probe measurement modes such as lateral force microscopy (LFM), force modulation microscopy and phase imaging are more powerful techniques for measuring frictional forces and viscoelasticity properties of the materials beyond surface topographic measurements [7]. In this work, some of the superior features of both these ellipsometric and AFM techniques have been employed to investigate oxygen pressure dependent optical and structural properties of this novel Gd_2O_3 optical films deposited through reactive electron beam evaporation process.

Gadolinium oxide (Gd_2O_3) has several demanding applications as potential gate dielectric material in the semiconductor industry [8–12]. Most recently, Gd_2O_3 material has drawn a special attention as a high index optical coating material due to its large band gap and extended spectral transparency over ultraviolet to infrared [13]. Favourable optical and topographical properties have made this material more important for making multi-layer optics in the ultraviolet region of the spectrum by combining with an appropriate low index material such as SiO_2. In spite of such potentials, no dedicated and systematic studies have been done for its structure and topography related optical properties. The stoichiometry and related topography in GdO_x thin films for MOSFETs deposited by MBE technique is reported to remain almost constant over a range of substrate temperatures and rates of the deposition [9]. However, in spite of its strong oxygen affinity, there are no oxygen related studies carried out on this film deposited by reactive physical vapour deposition. This is the prime reason that the present investigation is dedicated to the study the effect of oxygen pressure on this novel thin film material with a special interest to optical coating applications. In this paper, we have studied the structural and optical behaviour of this material with respect to reactive oxygen pressure through phase-modulated spectroscopic ellipsometric and multi-mode AFM. During these studies, we have discovered some excellent co-relationships between optical and structural properties derived through these advanced characterisation techniques. Both techniques depicted very similar trends in the oxygen dependent film properties and this has emphasised the reliabilities and aptness in the bi-layer ellipsometric modelling and the AFM multi-mode measurements and subsequent grain analysis.

2. Experimental

For the present studies, Gd_2O_3 thin films have been deposited by reactive electron beam evaporation at different oxygen partial pressures by keeping the rate of deposition and substrate temperature constant. The oxygen partial pressure has been varied from 0.5×10^{-4} to 2×10^{-4} mbar. The rate of deposition and substrate temperature are kept 1 nm/s and 70 °C, respectively during this deposition process. The purpose of keeping low ambient substrate temperature is that this optimised value gives a higher band gap as shown in the plot of energy versus square of the absorption coefficient (Fig. 1). Such a

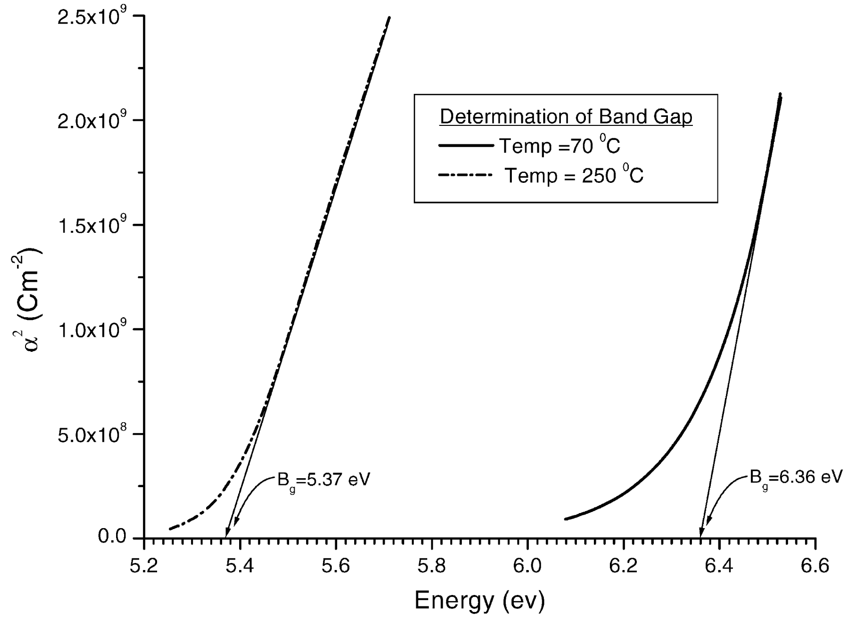

Fig. 1. Plot for comparison of direct band gaps of gadolinium oxide thin films deposited at two different substrate temperatures of 70 and 250 °C, respectively. The rate of deposition and oxygen pressure are kept at 1.0 nm/s and 1.0×10^{-4} mbar. The lower substrate temperature of 70 °C has yielded a higher band gap of 6.36 eV for Gd_2O_3 films in comparison to a higher substrate temperature of 250 °C where the band gap value achieved is only 5.37 eV.

large band gap is an essential as well as preferred criterion for ultraviolet applications. Also at low temperature, the material can be compatible with wide varieties of substrate materials. The thickness of the thin films has been monitored through both optical (Leybold's OMS 2000) and quartz crystal (Leybold's XTC/2) monitors. The residual gases in the coating chamber have been analyzed by Pfeiffer's Prisma-200 quadrupole mass spectrometer. The deposited thin films have been analyzed through spectroscopic phase-modulated ellipsometry for its optical properties using Jobin Yvon's UVISEL ellipsometer. This spectroscopic ellipsometer has a wavelength in the range of 250–1700 nm and also has a goniometer with selectable angle of incidence in the range of 40–90°. A realistic two-layer thin film growth model has been used to fit the ellipsometric measurements as shown in Fig. 2. AFM has been employed to study the surface topographic and microstructural properties of the thin films through topographic and lateral force measurements using NT-MDT's Solver P47H multi-mode scanning probe system.

3. Results and discussion

In the present experiments, both ellipsometry as well as multi-mode AFM have provided extremely valuable information related to optical and microstructural properties of Gd_2O_3 films deposited under various oxygen pressures. Although both techniques use very different methodologies in probing the surfaces and interfaces, we could find strong co-relationships in the results with respect to their optical and structural properties.

The acquired ellipsometric data for various thin film samples were analyzed using a simple bi-layer model incorporating both columnar structure and roughness in the concept as shown in Fig. 2. Effective medium analysis (EMA) techniques have been employed to look into void fraction as well as grain size distributions while computing the effective dielectric function ε, which is as follows [14]:

$$f_s \frac{\varepsilon_s - \varepsilon}{\varepsilon_s + 2\varepsilon} + f_v \frac{\varepsilon_v - \varepsilon}{\varepsilon_v + 2\varepsilon} = 0 \quad (1)$$

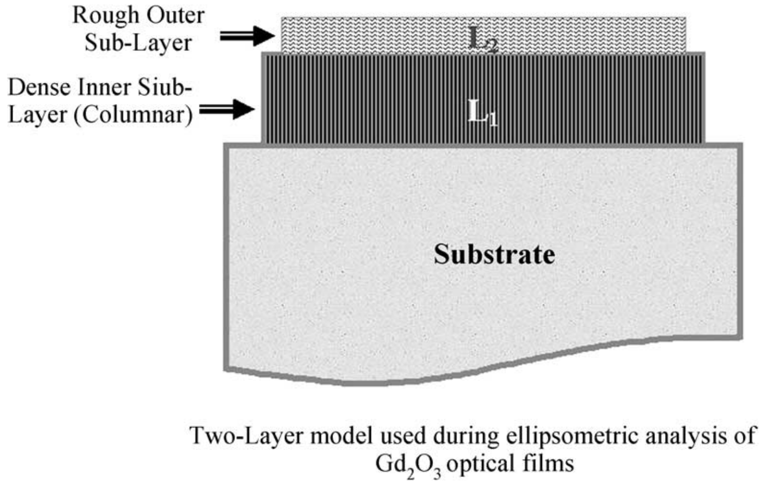

Fig. 2. Bi-layer model used for ellipsometric modelling of gadolinium oxide thin films. In this model, L1 represents a dense columnar sub-layer and L2 represents a rough void prone surface sub-layer.

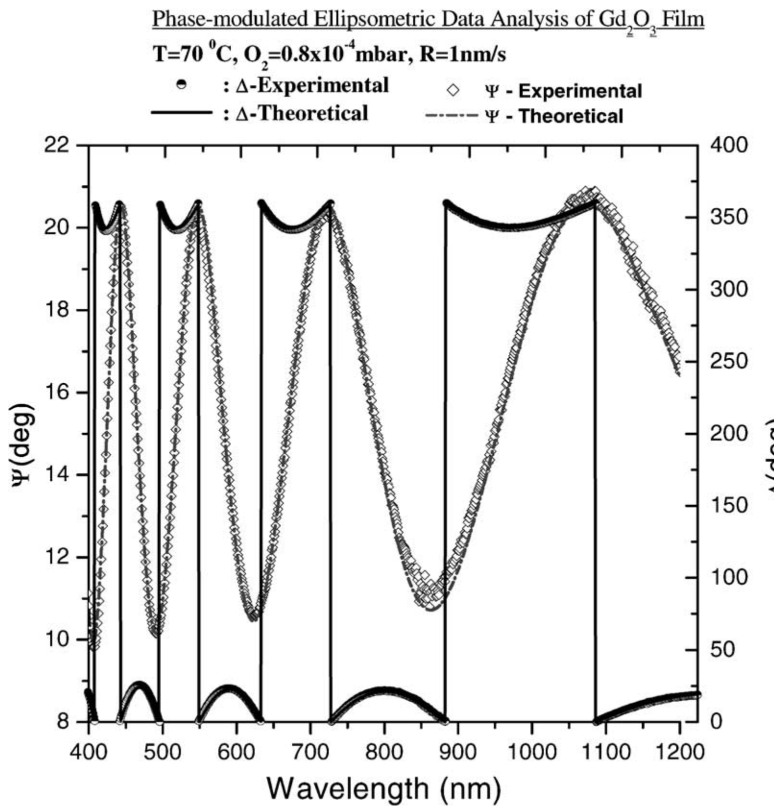

Fig. 3. Plots portraying experimental and theoretical ellipsometric parameters Ψ and Δ that are obtained by phase-modulated spectroscopic ellipsometry. The theoretical spectra are generated through a thin film bi-layer model using both columnar structure and surface roughness in the computation.

where ε_s, ε_v, f_s and f_v are the dielectric functions and the volume fractions of isotropically averaged grains and voids. A typical ellipsometric data analysis has been depicted in Fig. 3 for a Gd_2O_3 thin film sample deposited under our optimum oxygen pressure of 0.8×10^{-4} mbar. Both the experimental ellipsometric parameters Ψ, Δ and their fitted curves have been depicted in this figure. The goodness of the fit can be very well seen in the plot, which has well supported our bi-layer growth model for these films. The spectral mean refractive index profiles for the films deposited under various oxygen partial pressures are depicted in Fig. 4. It is clear from this figure that variation of oxygen pressure has distinct influences on the spectral mean refractive indices. This plot also shows that a better index profile has been obtained at an optimum oxygen pressure of 0.8×10^{-4} mbar. Fig. 5 portrays the variation of mean refractive index with respect to various oxygen pressures at the spectral wavelength of 600 nm. This figure provides a good insight in realising the effect of oxygen pressure on refractive index. Like Fig. 4, this figure also indicated that the maximum mean refractive index value is achievable for the films deposited under the oxygen pressure value of 0.8×10^{-4} mbar. The plots shown in the Fig. 6 show the variation of refractive indices of inner dense sub-layer 1 (L1) and the outer rough sub-layer 2 (L2). The data values are spline-fitted to obtain a smooth functional dependence. As it can be seen from this figure, the mean index derived from the EMA modelling is dominated by the index of the inner void-free and thick L1 sub-layer. The refractive index of the thin outer rough sub-layer L2, is strongly influenced by its local compositions and microstructures. So, the surface sub-layer L2 primarily decides topographical features of the present thin film samples. The functional dependence between refractive index and the microstructure can be conveniently derived using both Clausius–Mossotti and Lorenz–Lorenz relationships as follows [15]:

$$n = \left(1 + \frac{8\pi\rho N_A}{3}\sum_j \frac{P_j\alpha_j}{W_j}\right)^{1/2} \times \left(1 - \frac{4\pi\rho N_A}{3}\sum_j \frac{P_j\alpha_j}{W_j}\right)^{-1/2} \quad (2)$$

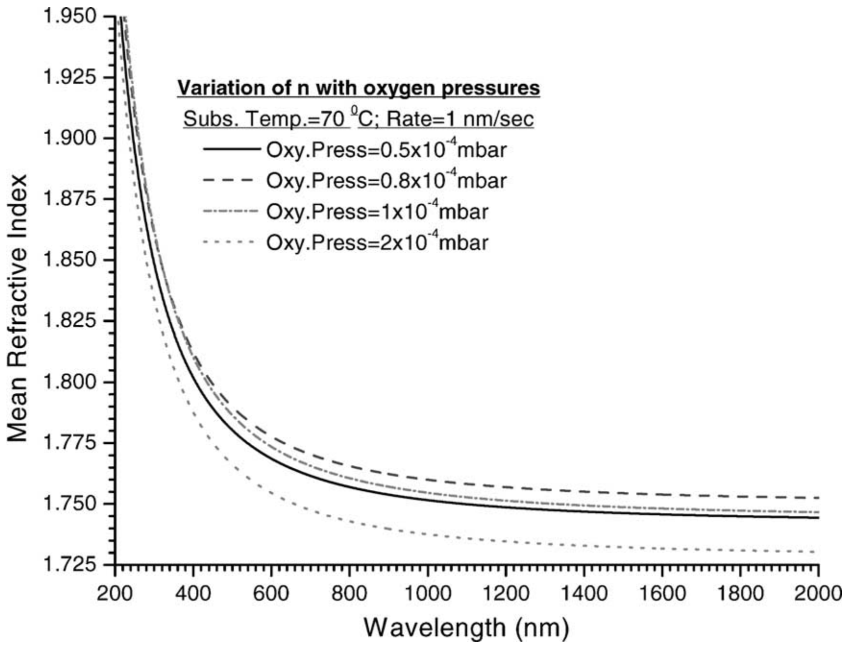

Fig. 4. Spectral mean refractive indices of electron beam deposited gadolinium oxide thin films at various reactive oxygen pressures. During this deposition, substrate temperature and deposition rate are kept 70 °C and 1.0 nm/s, respectively.

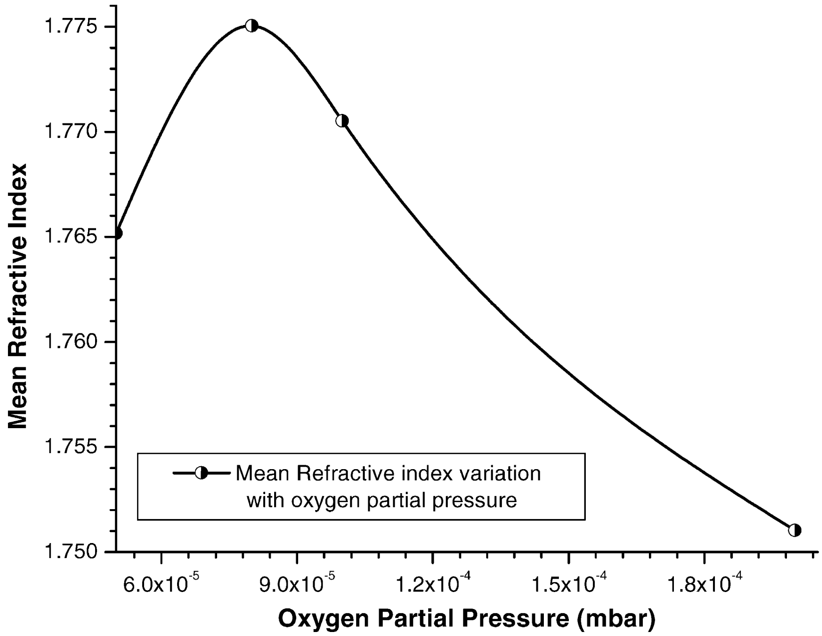

Fig. 5. Variation of mean refractive index of gadolinium oxide thin film with respect to various reactive oxygen pressures measured at the spectral wavelength of 600 nm. The data are spline interpolated for realising a smooth functional dependence.

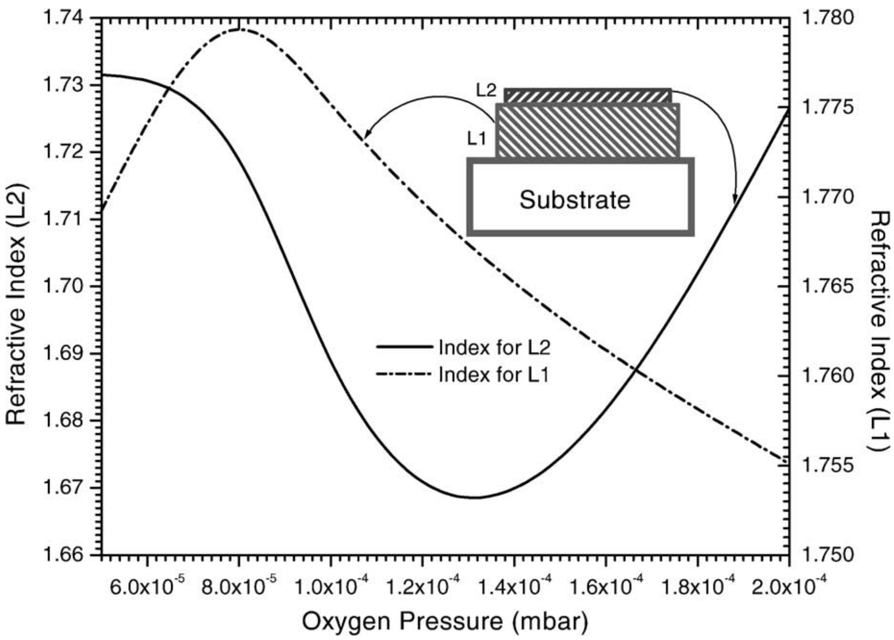

Fig. 6. Variation of refractive index of inner dense columnar sub-layer (L1) and outer rough sub-layer (L2) with respect to oxygen pressures, which are obtained through ellipsometric bi-layer modelling. The data are spline interpolated for realising a smooth functional dependence.

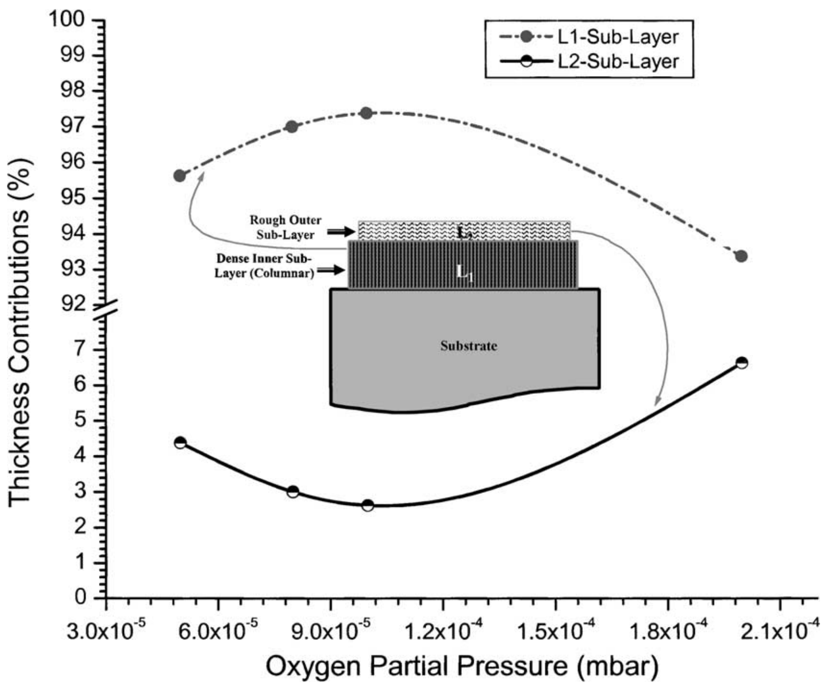

Fig. 7. Variation of percentage of thickness contributions of inner sub-layer (L1) and outer rough sub-layer (L2) with respect to various oxygen pressures. These results are obtained through ellipsometric bi-layer modelling and with spline interpolation.

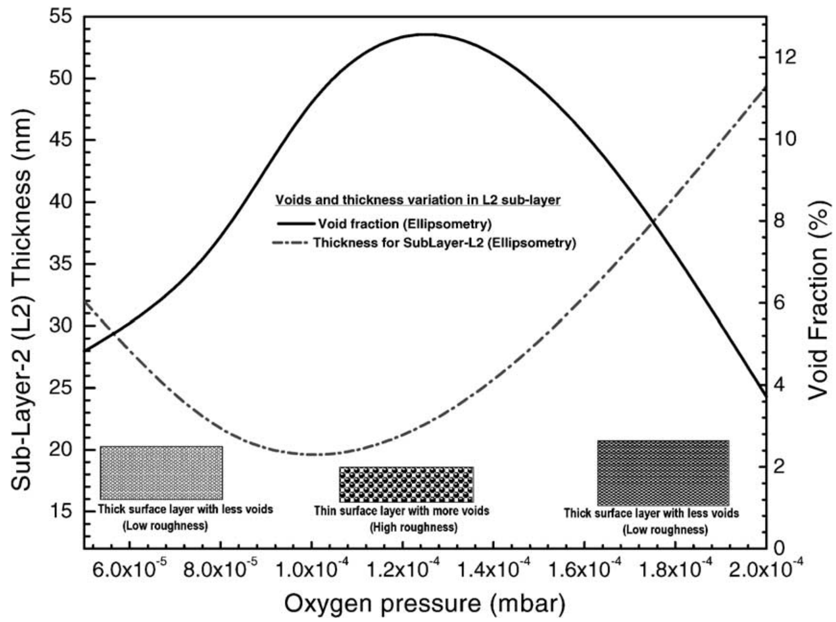

Fig. 8. Variation of void fraction percentage in outer rough sub-layer (L2) and corresponding physical thickness with respect to oxygen partial pressures obtained from ellipsometric data analysis. The data are spline interpolated for realising a smooth functional dependence.

where n is the refractive index, α_j the electronic polarisability, N_A is the Avogadro's number, W_j the molecular weight, ρ the density, and P_j the weight fraction of the species j in the thin film sub-layer.

It can be seen from this Fig. 6 that the refractive index of the rough sub-layer (L2) varies very differently from that of L1. Fig. 7 portrays the percentage of thickness contribution of each sub-layer obtained from ellipsometric modelling. For all the sample films, the outer rough-layer thickness is very small in comparison to the inner dense sub-layer. This implies that the mean refractive indices governed by the film microstructure are more influenced by sub-layer L1, whereas, the sub-layer L2 dominates in the topography or surface roughness. Our measurements have shown that relatively smooth topographies are obtained at the lower and higher values of our experimental oxygen pressures. Fig. 8 portrays the void fraction obtained from the ellipsometric EMA modelling and corresponding thickness of the rough outer sub-layer (L2). In this figure, behaviour of both the void fraction and the thickness of L2 sub-layer can very well explain the roughness variation with respect to the oxygen pressure. At low oxygen pressure, the sub-layer L2 is relatively thick with less voids and so also is the case for higher oxygen pressures. Such conditions unambiguously lead to a smooth surface topography. The case is opposite for the in-between values for the oxygen pressure, where L2 sub-layer is thin with more voids. This is the reason that such conditions give a relatively rough topography, which also is well supported by our AFM measurements. In Fig. 9, the functional behaviour of the surface roughness obtained from topographic measurements and the refractive index of L2 sub-layer under various oxygen pressures are shown for comparison. The refractive index is known to be a representative of the density of the thin film and also is a strong function of the microstructure. Such an aspect is clearly visible while comparing these two measurements in this Fig. 9. Samples with low roughness values as obtained from AFM measurements have shown higher index in the surface sub-layer and the vice versa.

The limitation of ellipsometry is highlighted while probing the detailed microstructure correlated topographies of the thin film surfaces. In such cases, AFM techniques prove their advantages to derive the relevant information through various modes of their measurements. In the present case, both topographic and lateral force microscopic imagings through contact

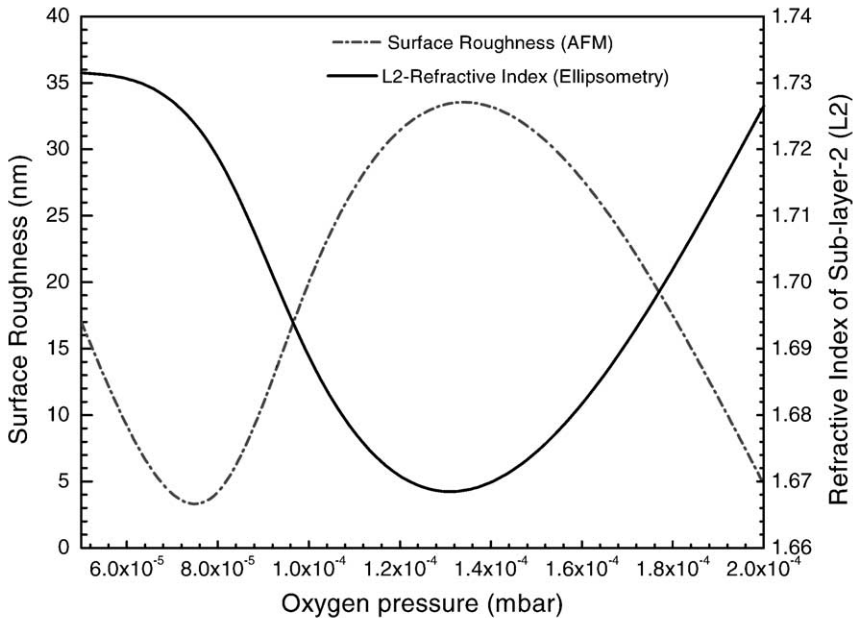

Fig. 9. Variation of surface roughness measured by AFM and refractive index of the rough sub-layer (L2) obtained from ellipsometric modelling. The microstructural dependence of the refractive index can be very well established by comparing these two measurements.

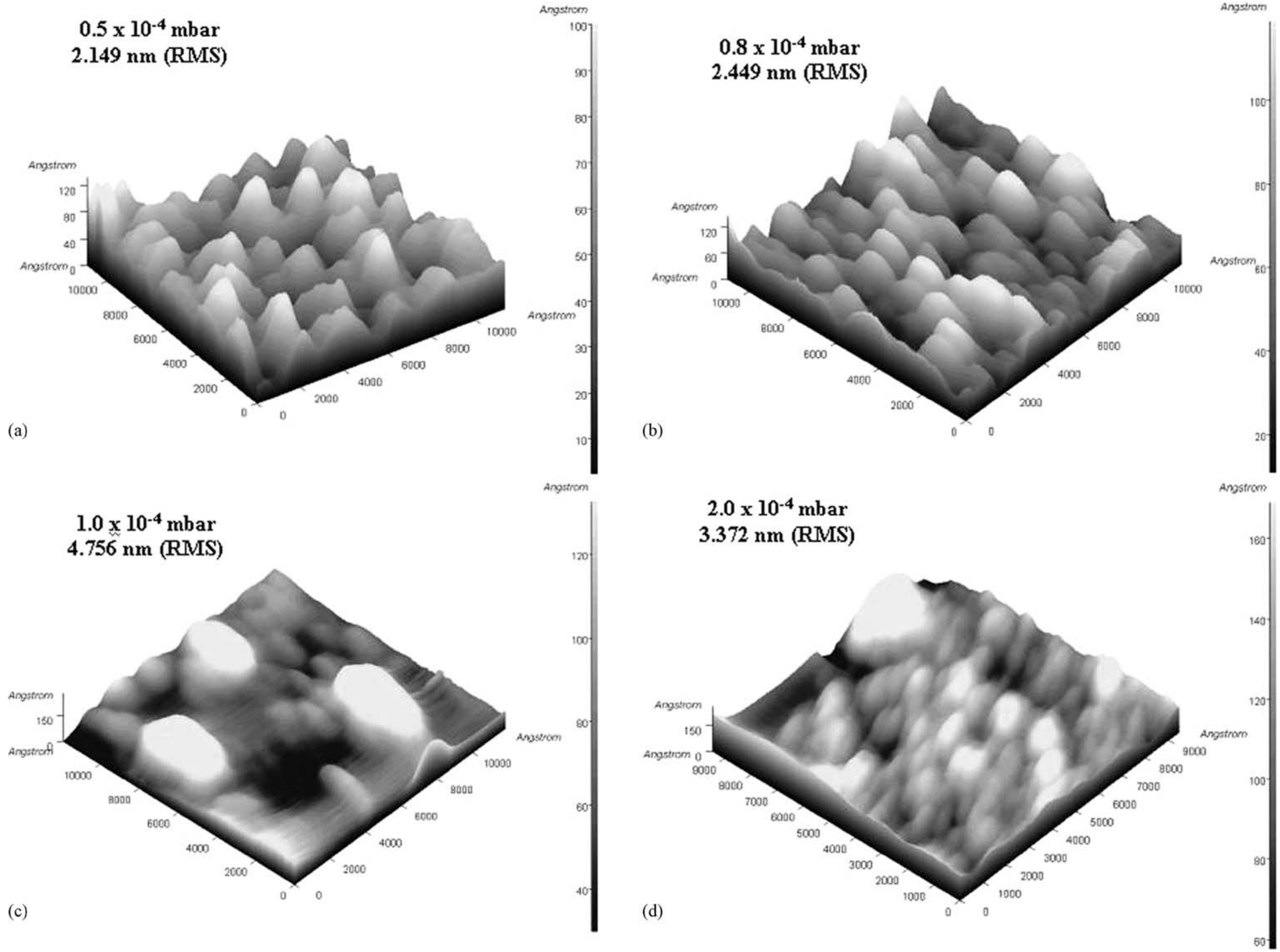

Fig. 10. Surface topographies of gadolinium oxide thin films having RMS roughness values of 2.149, 2.449, 4.756 and 3.372 nm under the oxygen pressures of (a) 0.5×10^{-4} mbar, (b) 0.8×10^{-4} mbar, (c) 1.0×10^{-4} mbar and (d) 2.0×10^{-4} mbar, respectively. In this plot, deposition rate and substrate temperature are kept constant at 1 nm/s and 70 °C, respectively.

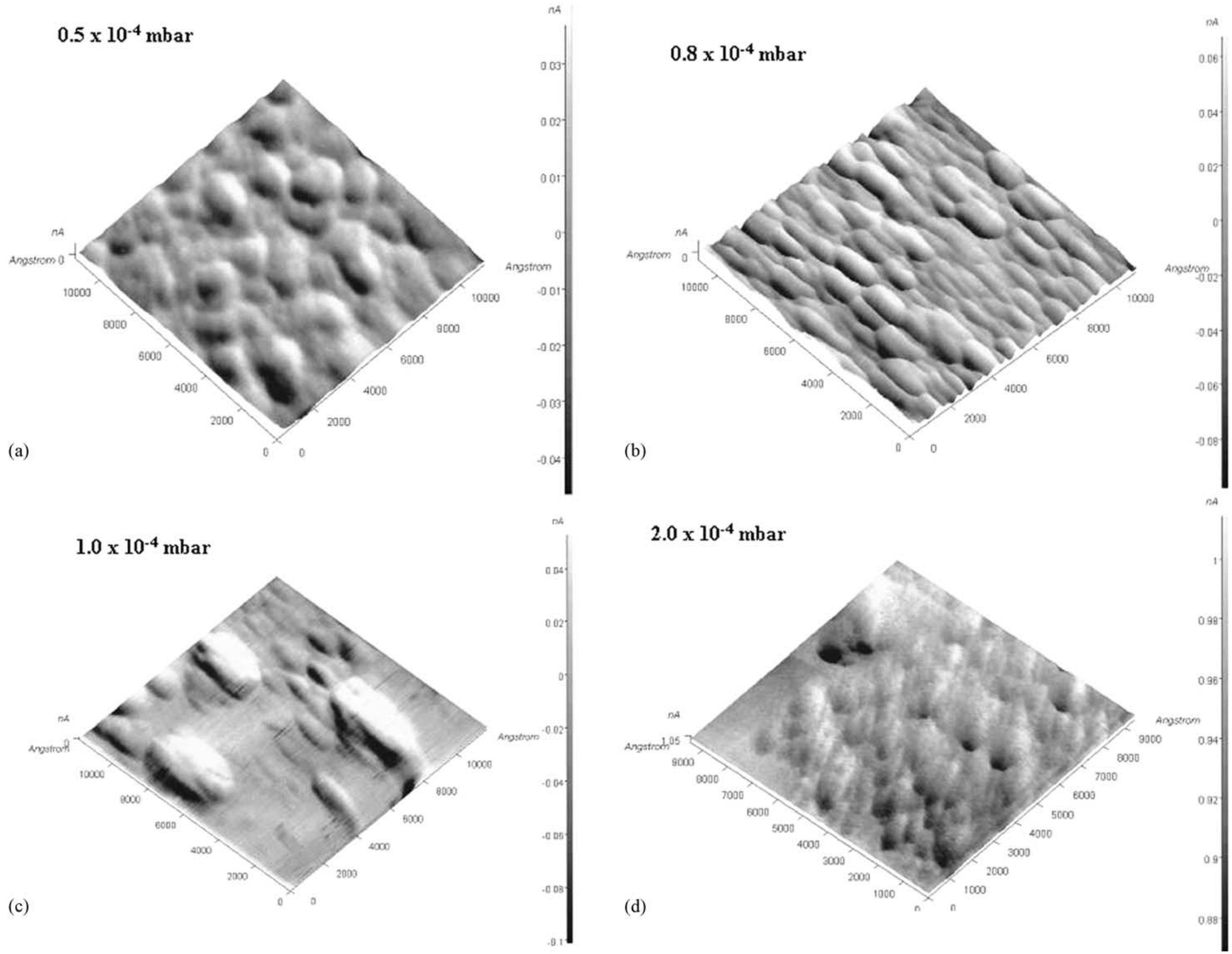

Fig. 11. Lateral force images of gadolinium oxide thin films at four different oxygen pressures of (a) 0.5×10^{-4} mbar, (b) 0.8×10^{-4} mbar, (c) 1.0×10^{-4} mbar and (d) 2.0×10^{-4} mbar, respectively. In this plot, deposition rate and substrate temperature are kept constant at 1 nm/s and 70 °C, respectively.

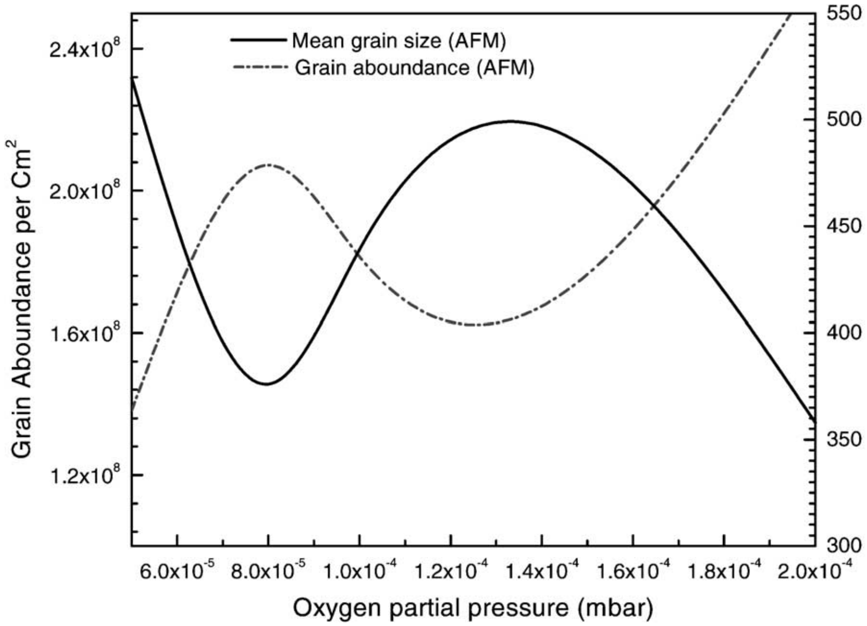

Fig. 12. Plots portraying variations of surface grain abundance per square centimetre and mean grain size obtained from surface topographic grain analysis with respect to various oxygen partial pressures. The data are spline interpolated for realising a smooth functional dependence.

mode measurements have been utilised to probe the sample surfaces. An advanced grain analysis module has been employed to derive the detailed thin film surface microstructure.

AFM pictures for topography and LFM for the films deposited under four different oxygen pressures have been depicted in Figs. 10 and 11 respectively. It can be seen from topographic measurements (Fig. 10) that relatively small and regular grains are obtained both at optimum and higher values of the oxygen pressures. This demonstrates a very similar trend with respect to the void fractions obtained from ellipsometric measurements (Fig. 8). Topographical analysis mostly depicts the roughness as well as grain size distributions, where as LFM identifies and maps relative differences in surface frictional characteristics. It is one of several techniques developed as extensions to the basic topographical mapping capabilities of scanning probe microscopy (SPM). LFM is particularly useful for differentiating among materials on surfaces [16]. In the present application, it can be related to stoichiometric fluctuations in the surface of the films. LFM, therefore, has the advantages of identifying surface compositional differences where the materials have differing frictional characteristics and the topography is relatively undifferentiated. It should be noted, however, that these differences could be obscured by rough topography or by contamination overlying the actual sample surface. The LFM image of thin film also often identifies individual grains not seen in the topographical image. In our present analysis, localised defects in the sample deposited under higher oxygen pressure unnoticed in the topographic measurements are highlighted in LFM modes. Fig. 12 depicts surface grain abundance and relative grain sizes in the sample surfaces prepared under various oxygen pressures. As expected, the plot characteristics are complementary indicating sample with small mean grain size has more grain abundance and the vice versa. Also, smaller mean grain sizes can be attributed to the better refractive index values because of the large resultant packing density of such grains. Results of this measurement can be very well compared with the L2 sub-layer refractive index plot in Fig. 6, which is acquired through the ellipsometric data analysis. The lower refractive indices (L2 sub-layer) obtained at intermediate values of the reactive oxygen pressure can be very well related to the lower grain abundance and larger grain sizes.

4. Conclusion

Gadolinium oxide thin films deposited by electron beam evaporations have shown very interesting optical and structural properties under various reactive oxygen pressures. Phase-modulated ellipsometry and multi-mode AFM have been used to characterise the optical and microstructural properties of these sample films. Several interesting co-relationships among the refractive index, topography and microstructures have been established from the data acquired through these two independent characterisation techniques. Both the techniques appropriately point out to an optimum value of the oxygen pressure that can lead to a film with dense microstructure and better refractive index value. Thin film bi-layer model used in ellipsometric data analysis of the present Gd_2O_3 films also justified its suitability when compared with AFM multi-mode measurements.

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