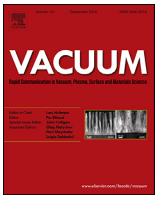
Vacuum 134 (2016) 110–119

Contents lists available at ScienceDirect

Vacuum

journal homepage: www.elsevier.com/locate/vacuum



Surface characterization of magnesium fluoride thin films prepared by a fluorine trapping based non-reactive sputtering technique

Rajnarayan De [a], S. Maidul Haque [a], S. Tripathi [a, *], K. Divakar Rao [a], C. Prathap [a], Mohit Kumar [b], T. Som [b], N.K. Sahoo [c]

[a] Photonics and Nanotechnology Section, Atomic and Molecular Physics Division, Bhabha Atomic Research Centre Facility, Visakhapatnam 530012, India
[b] Institute of Physics, Sachivalaya Marg, Bhubaneswar 751 005, Odisha, India
[c] Atomic and Molecular Physics Division, Bhabha Atomic Research Centre, Mumbai 400085, India

ARTICLE INFO

Article history:
Received 6 April 2016
Received in revised form
7 October 2016
Accepted 8 October 2016
Available online 11 October 2016

Keywords:
MgF_2 thin films
RF magnetron sputtering
Ellipsometry
Atomic force microscopy
Surface correlation functions
Roughness evaluation

ABSTRACT

Successful deposition of magnesium fluoride thin films by a non-conventional magnetron sputtering technique is reported here followed by the analysis of their optical, morphological and structural properties. The drawback in the external supply of health hazardous fluorinated gases in the context of fabricating fluoride films by conventional sputtering processes was completely eliminated by trapping the dissociated fluorine gas inside the chamber during deposition. The dependencies of basic thin film properties stated above on magnetron energizing power were investigated. Qualities of surface structures were analyzed on the basis of surface roughness and surface correlation function parameters. A qualitative correlation of film morphology with optical properties of such fluoride films was observed in the present study. Film growth rates were found to have great importance in deciding the surface topography of the films. Careful investigation of film structure clearly revealed a remarkable increase in crystallite size with the increase in sputtering power. The composition of the film is maintained throughout the studied power range as seen by X-ray photoelectron spectroscopy. Finally, optimum sputtering power for film deposition was decided by taking into consideration the quality in surface structure together with optical quality of the films.

1. Introduction

Magnesium fluoride (MgF_2) is a technically very important low index material in UV-VUV optical coating applications due to its high transparency and low optical loss in this wavelength range [1]. These films are also very promising in deep UV laser optics applications where high laser induced damage threshold is a stringent requirement [2]. Another important application is in the wideband antireflection (AR) coatings, where it can be used to overcome the limitations of residual reflectance in wide band AR coatings arising due to the lack of availability of low refractive index materials in nature [3]. Experimentally, it could be seen that glancing angle deposition (GLAD) of nanoporous MgF_2 thin films with very low refractive index (1.16) as a top surface over interference multilayer stacks completely fulfils this vacancy [4]. By depositing single layer of MgF_2 film, one can adjust the transmittance of AR coatings by varying the layer thickness and thus a promising optical structure can be fabricated to be used in high power laser applications [5]. MgF_2 films are also being used as a buffer layer for Pd in hydrogen sensors due to their high transparency [6]. Similarly, these films find application in multilayer in combination with indium tin oxide (ITO) for solar cell applications [7], in combination with Ag for electromagnetic shielding applications [8,9] and as an over layer on Al mirrors to enhance the reflectance of these mirrors in the vacuum UV region [10] to be used in free electron lasers and spectroscopy [11].

In past, various deposition methods have been applied for preparing MgF_2 thin films including thermal evaporation [11–13], Ion beam sputtering [14,15], e-beam evaporation [16,17], molecular beam evaporation [18], Ion-beam assisted deposition (IBAD) [19], Plasma ion assisted deposition (PIAD) [20] etc. However, it has been found that the characteristics of these films strongly depend on the deposition method itself [1]. Proper stoichiometric MgF_2 film deposition can be made by evaporation technique without addition of reactive gas, but the deposited films have low packing densities leading to the adsorption of water in the film [21,22]. The

---

* Corresponding author.
E-mail address: shilpatripathi75@gmail.com (S. Tripathi).

http://dx.doi.org/10.1016/j.vacuum.2016.10.009

fabrication of these fluoride films by chemical method has also not been widely accepted due to the handling of hazardous fluorine precursors HF or F_2 gas [23]. In addition, the films prepared by chemical route suffer from low quality [23,24] in terms of mixed contribution from MgF_2 as well as from the precursors used.

Generally, sputtering is considered to be superior to other available PVD techniques due to its several advantages over them which include better adhesion on the substrate, film composition close to the bulk etc. Over other sputtering techniques, magnetron sputtering seems to be a better option for depositing MgF_2 films because of high deposition rate (approximately one magnitude higher) [25] and low substrate heating [26]. However, with sputtering also, it is very difficult to achieve proper stoichiometric MgF_2 films because of dissociation of MgF_2 followed by fluorine exhaust through vacuum pump resulting in fluorine deficiency in the deposited films [27]. A few reports have addressed this issue and hence research was performed on the use of reactive gas mixture of CF_4+O_2+Ar [27], SF_6 and F_2 gas [28]. In all these studies, either the Mg/F ratio was not increased due to inclusion of carbon and oxygen or the index was high. However, the problem in poor stoichiometry and high refractive index of the films prepared by a reactive gas mixture of $CF4+O_2+Ar$ was later removed by Mertin et al. [29] by focussing on $CF4:O_2$ ratio instead of CF_4: Ar ratio. But, the importance of optimal flow ratio of fluorinated gas and sputtering gas for the preparation of good stoichiometric films cannot be neglected. In addition, it is also possible to prepare MgF_2 films without the introduction of hazardous fluorinated reactive gasses (which are costly and also not readily available) but with the use of some innovative non-conventional method [1,28]. In this work, we have relied on this particular non-conventional magnetron sputtering technique based on fluorine trapping for the deposition of MgF_2 films [30].

Although fluorine trapping is a good alternate technique, the effect of deposition parameters on the quality of films is scanty. The present communication is therefore focused on exploring the effect of magnetron energizing power on the morphological, optical and structural properties of the F_2 trapped RF magnetron sputtered MgF_2 films. More emphasis is given on the quality of surface structure of these films along with optical quality because of suitability of these materials in optical coatings as well as in catalytic processes [31] depends on diffuse scattering losses inside them in addition to good optical properties. The surface properties of all the samples have been studied along with the quality of films with respect to various morphological parameters. The variation of surface properties is also correlated with the optical and structural properties of the films.

2. Experimental

2.1. Sample preparation

Magnesium fluoride thin films with thickness of ~22–25 nm were deposited by RF magnetron sputtering with MgF_2 target (Cerec, 99.9% purity) having diameter of 76 mm and thickness of 5 mm. Prior to each deposition, the chamber was evacuated to a base pressure of ~6×10^{-6} mbar by employing a turbo molecular pump backed by a rotary pump. The target was pre sputtered for ~15 min at 100 W RF power to remove surface contamination, if any. All the MgF_2 films were deposited on 1 inch Si (111) substrates. Six samples have been deposited at an optimized target to substrate distance of 3 cm for various magnetron energizing powers visualising 50 W, 80 W, 120 W, 160 W and 250 W.

Thin film deposition was performed under a non-conventional experimental technique, in which plasma was ignited in the presence of argon as sputtering gas and soon after the ignition; the argon gas flow inlet was completely closed to get self-sustained plasma. Chamber pressure was taken down to the minimum pressure (typically ~ 5×10^{-3} mbar) the plasma can sustain without gas inflow to ensure low contamination of argon in the films. Then slowly the gate valve of the chamber was completely closed so that the decomposed fluorine from the target will not escape from the chamber. This process is termed as "*fluorine trapping*". The chamber pressure started to increase as soon as the gate valve was closed and a monotonic increase of the chamber pressure was recorded with time. The chamber was isolated for 25 min so that sufficient fluorine gas can be gathered inside the deposition chamber before deposition. Then the deposition was started by opening the cathode shutter when the pressure reaches ~3×10^{-2} mbar and was allowed to continue till ~9×10^{-2} mbar pressure (at which the deposition rate drastically reduces) which imposes the thickness limitation on the fabrication of optical coatings.

2.2. Characterization

The optical properties of all the samples were measured by using a rotating polarizer spectroscopic ellipsometer SEMILAB GES5-E in the wavelength range of 200–1100 nm. The angle of incidence (70°) was decided based on the Brewster's angle measurement of the substrate-film assembly to achieve the maximum sensitivity of the measurement [32]. Spectroscopic ellipsometry is a non-destructive and widely used technique for the accurate measurement of optical properties of thin films. Basically, the instrument records the change in polarization state of the plane polarized incident light upon reflection from the sample. The measured data includes the variation in amplitude ratio (ψ) and phase difference (Δ) of two electric field vector components of the incident light with wavelength (λ), which is related to the ratio (ρ) of r_p and r_s, the reflection coefficients (complex numbers) for the p and s components of the wave respectively, as per the following formula:

$$\rho = r_p/r_s = tan(\psi)exp(i\Delta) \tag{1}$$

Fitting of the measured data with a properly chosen dispersion model is required to extract the optical and physical parameters of a thin film sample.

For the structural characterization, grazing incidence X-ray diffraction (GIXRD) measurements of the as-grown samples were performed on Rigaku made Smartlab X-ray diffractometer by using Cu Kα ($\lambda = 1.5418$ Å) as incident radiation at grazing angle of 0.5°. The diffracted beam intensity was recorded in the diffraction angle (2θ) range of 20–90° in steps of 0.01°. The same instrument was used for X-ray reflectivity (XRR) measurements in 2θ range of 0–6° in steps of 0.01°.

Surface topography of the films was measured in order to investigate the modifications in surface properties with increase in sputtering power by using ex situ atomic force microscopy (AFM) (MFP3D, Asylum Research, USA). Silicon probes with ~10 nm tip diameter were used for imaging. The raw morphological data were analyzed by using Gwyddion SPM data visualization and analysis tool, version 2.42 [*http://gwyddion.net/*] together with WSxM software application, version 5.0 Develop 7.0, Nanotec Electronica S.L. [33] to extract various important morphological properties such as root mean square (rms) surface roughness, correlation length, mean cluster size, mean inter-cluster separation etc. The surface properties of MgF_2 thin films have been investigated in past by several groups [15,17,34]. Comparative investigations were performed to study the influence of deposition process and post deposition treatment parameters on the surface morphology and bonding structure etc. Thus, AFM is a well-established method to probe the surface structure of MgF_2 films and hence it has been