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Design and fabrication of multi-layers antireflection coating consisting of MgF_2 and SiO_2

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ABSTRACT

In this research, MgF_2 and SiO_2 thin films were prepared by the magnetron sputtering method on glass and ITO substrates. The crystal structure, morphology, and antireflection performance of the coatings were characterized using X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), and ultraviolet spectrophotometry (UV-vis) techniques, respectively. Furthermore, by utilizing both experimental characterization and optical film design tools, the best experimental parameters for every coating were identified. FESEM images confirmed proper growth of the layers on the substrates. EDAX analysis revealed that the manufactured layer consisted of Magnesium fluoride and silica. The study of optical properties demonstrated that the average transmission in the 400-1000 nanometer range exceeded 99%, indicating good agreement with theoretical results. Furthermore, the use of ITO as the substrate reduced the bandgap.

1. Introduction

Antireflective coatings are used in various optical instruments, such as telescopes, lasers, display screens, solar cells, military equipment, and etc. The reduction of reflected light improves the performance of these instruments [1, 2]. The amount of light reflected from the surface of an object depends on its refractive index. To minimize reflection, the refractive index of the surface should as close as possible to the refractive index of air [3]. Among different materials, Silica with a refractive index of 1.45, Aluminum with a refractive index of 1.65, and Titania with a refractive index of 2.3 are most commonly used. It should be noted that Magnesium Fluoride also has a refractive index of 1.37 but is not widely used [4]. The number of coating layers is an effective factor in building antireflective films. Antireflection coatings can be made in single-layer, double-layer, and multi-layer form. Single-layer coatings, with a thickness of one-fourth of the wavelength of the incident light, are the most commonly used anti-reflective coatings in solar cells. Since single layer coatings are non-reflective only at a single wavelength, various attempts for antireflection coatings improvement in the formation of multilayer thin films have been carried out. Two-layer and multi-layer coatings are used for wider wavelengths to address issues such as increased light transmission. Two-layer coatings exhibit a V-shaped transmission curve, and the thickness of each layer can be one-fourth or half of the incident light's wavelength. These coatings can achieve to 99% light transmission [5]. Two-layer and multi-layer coatings can either use one material with different structures for each layer or employ different materials. For example, SiO_2 and ZrO_2 two-layer coatings reduce the refractive index across a wider range of wavelengths [6]. Additionally, TiO_2 single-layer, SiO_2/TiO_2 two-layer, and SiO_2/SiO_2-TiO_2/TiO_2 multi-layer coatings have been successfully applied through a spinning process on single-crystal solar cells [7].

Magnesium Fluoride with the chemical formula MgF_2 is a chemical compound with 62. 3018g/mol molar mass. The

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crystal structure of MgF_2 is tetragonal. The SiO_2 chemical formula of silica is a chemical compound with 61.1 g/mol molar mass and a tetrahedral structure. Xin du et al. reported the hydrophilic three-layer silica antireflective coating mentioned above was built to create anti-fog characteristics and reached 98% transmission [8]. Remache et al. built a silica antireflective coating on a silicon solar cell; this coating resulted in a 9-percent increase in that solar cell's productivity [9]. Magnesium Fluoride and Silica can be deposited through various methods including sputtering [10], pulsed laser deposition [11], chemical vapor deposition [12], chemical bath deposition [13], photochemical deposition [14], pulsed electrochemical deposition [15], and electron gun [16, 17]. These methods are used to create dense and porous coatings [18]. Radio Frequency (RF) magnetron sputtering is considered as one of the best methods for preparing thin films. This method offers the possibility of controlling the growth conditions of layers, ensuring homogeneous and uniform deposition. Additionally, since the coating is performed in a plasma environment, it effectively cleans and roughens the surface of the substrate, enhancing adhesion. In preparing films by RF magnetron sputtering technique, some parameters are to be controlled. One of them is the type of substrate, which may affect the optical properties of the films. The present study aimed at investigating the structural, morphological, and optical properties of MgF_2/SiO_2 thin films prepared on different substrates. The reason for choosing MgF_2 and SiO_2 in this research is the right refractive index to pass in the visible spectrum and the choice of sputtering method due to the increase in adhesion and uniformity of the layers. The innovation of this article is that we were able to make a multi-layer antireflection coating with the use of this two-material material, with an optical transmittance of up to 99%. The main goal of this article is to design and manufacture a multi-layer antireflection coating with an optical transmittance of over 99%. Also, one of the other goals of this article is that the built coating has a good match with the designed coating. This coating may be used on solar cells in the future to increase sunlight.

2. Experimental

In this research, the coating of a four-layer structure (SiO_2 (85nm)/MgF_2 (150nm)/SiO_2 (70nm)/MgF_2 (200nm)) was prepared using RF magnetron sputtering. The sputtering system used was the Yarnikan Saleh MS model. The coating was applied to ITO and glass substrates. The SiO_2 and MgF_2 thin films were deposited using an RF magnetron sputtering process with MgF_2 and SiO_2 targets measuring 3 inches in diameter and 3 mm in thickness. The targets have 99.99% purity. Before Ar gas was injected, the chamber was first vacuumed to a pressure of 10^{-6} mbar. The working pressure was set at 0.7 Pa, and the RF power was kept constant at 95 Watts throughout the procedure. A schematic of how the layers are placed and their thickness is shown in Figure 1.

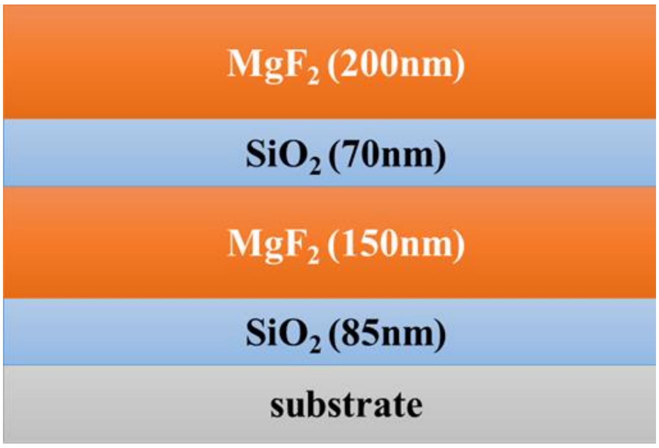

Fig. 1. A schematic of how the layers are placed and their thickness.

2.1. Characterization

Field emission scanning electron microscope FE-SEM (model Sigma 300 manufactured by ZEISS, Germany) was used to determine the thickness of layers and EDS analysis. Structural properties of the specimens were studied by X-ray diffraction (Bruker model D8 Advance, Germany) with quipped with Cu kα radiation source with λ= 1.5406Å, acceleration voltage of 40 kV, and electron current of 40 mA. Transmittans spectra were measured by a spectrometer (Perkin-Elmer Lambda750, USA) equipped with an integrating sphere.

3. Results and discussion

3.1. Morphological Properties

Fig. 2 (a) shows the cross-sectional FESEM images of magnesium fluoride and silica coatings for glass substrate. In this image, four layers of coverage can be seen. These images were analyzed using a digimizer software. In this research, the thickness of the layers was determined in the optimal state using Macleod software and the simplex method (85/150/70/200nm). The images show that the thickness of the first and the third layer (MgF_2) is 134 and 120.3 nm, respectively, and the thickness of the second and the fourth layer (SiO_2) is 79.3 and 68.36 nm, respectively. Figure 2 (b) shows the FESEM of the surfaces of the samples. This picture shows that the films have good surface properties. The roughness in the final layer can be attributed to the tension between the layers, especially the final layer, as well as the roughness on the substrate surface. In new research, anti-reflection coatings have been designed using two-layer and multi-layer models.

Energy-dispersive spectroscopy (EDS) was used to analyze the mass fraction of materials within the layers. Figure 3 illustrates the EDS results for the multilayer antireflection coatings. The analysis revealed that the layer consists of magnesium fluoride and silica. Figure 4 displays the distribution of elements across the coating, and Table 1 presents the mass fraction and atomic percent values for Mg, F, Si, and O. The mass percentages are approximately: Mg (8.14%), F (26.44%), Si (10.87%), and O (24.89%). The observed inconsistency in the total mass fraction (Mg+F+Si+O=70.34%) can be attributed to the presence of pollution in the device environment and carbon on the sample's surface during the calculation. The high percentage of indium in this compound may be due to contamination from the coating machine.

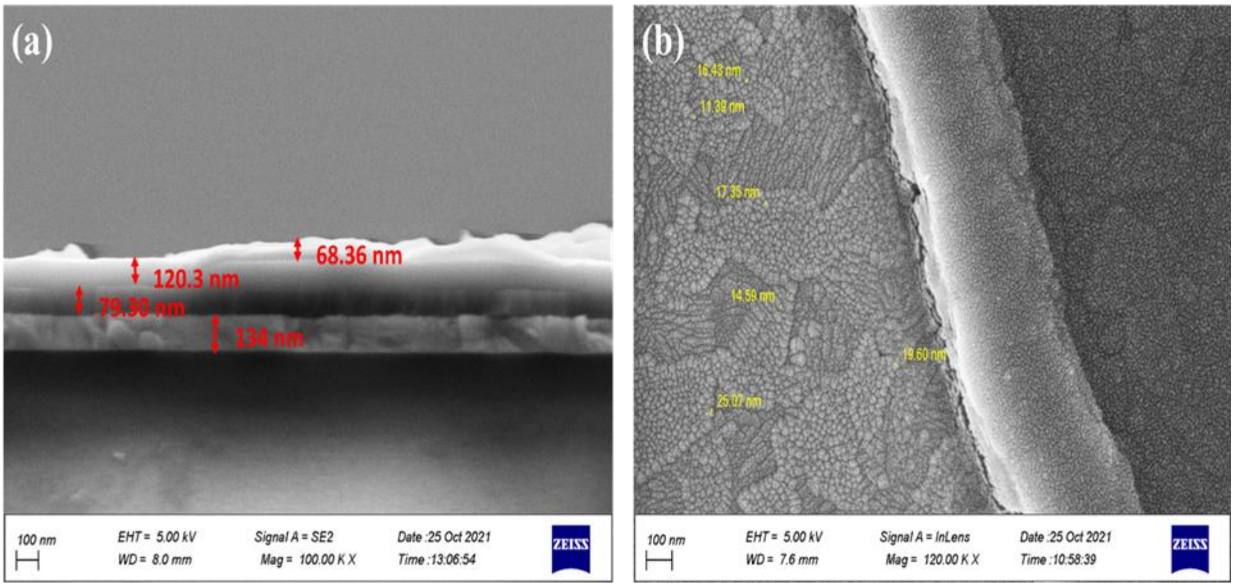

Fig. 2. FESEM (a) cross-section and (b) surface images of the quadruple-layer MgF_2 and SiO_2 coating on glass substrate.

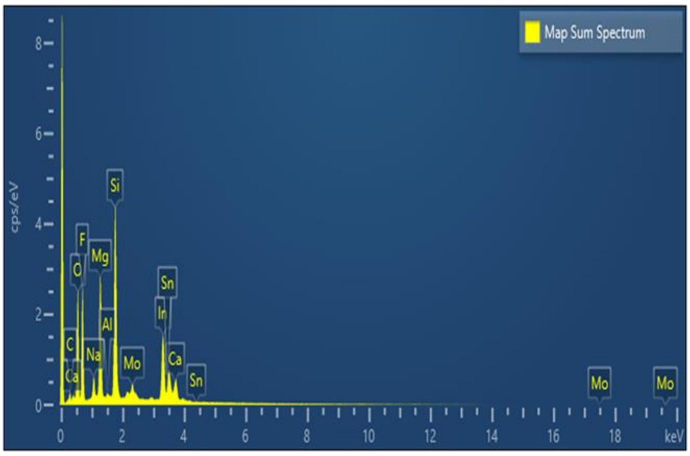

Fig. 3. EDS spectrum of the prepared sample with the quadruple-layer coating.

Table 1. Mass fraction and atomic percent of the prepared coatings.

Map Sum Spectrum				
Element	Line Type	Weight %	Weight % Sigma	Atomic %
O	K series	24.89	0.28	36.19
F	K series	26.44	0.28	32.38
Mg	K series	8.14	0.09	7.79
Si	K series	10.87	0.10	9.00
In	K series	18.13	0.20	3.67
Na	K series	1.79	0.06	1.81
Ca	K series	1.55	0.07	0.90
Mo	K series	2.90	0.16	0.70
Sn	K series	1.46	0.21	0.29
C	K series	3.68	0.36	7.13
Al	K series	0.16	0.03	0.13
Total		100.00		100.00

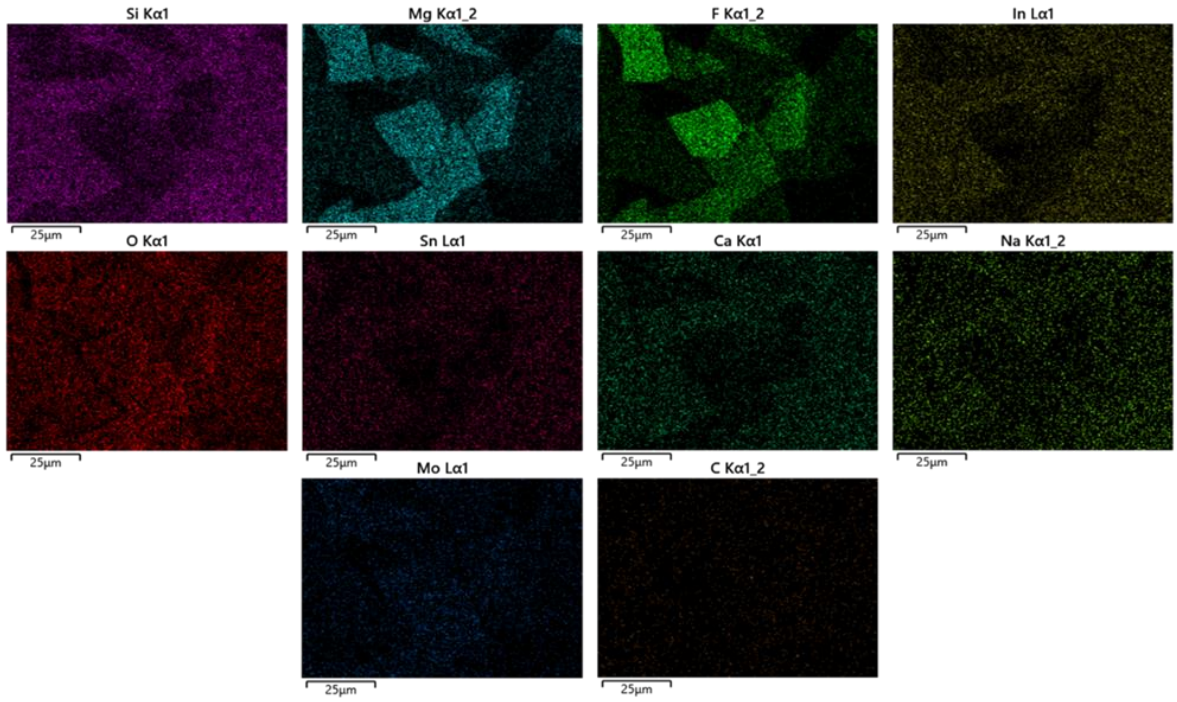

Fig. 4. Map image of the surface of the coating.

3.2. Structural Properties

The XRD analysis method is used to determine the properties of a crystalline structure, such as the geometry and structure of the lattice, crystal phase determination, crystallite size determination, strain analysis, and lattice deficiencies. In this method, extremely powerful x-rays are used to study the crystallographic direction. The basis of this method is Bragg's equation, where λ represents the wavelength, θ represents the angle of incidence, and d represents the distance between the two layers [19, 20].

$$2d\sin\theta = n\lambda \qquad (1)$$

The XRD pattern of MgF_2 and SiO_2 thin films is presented in Figure 5. MgF_2 has one crystalline structure lattice, which is tetragonal. SiO_2 is amorphous by nature, and its lattice structure is formless.

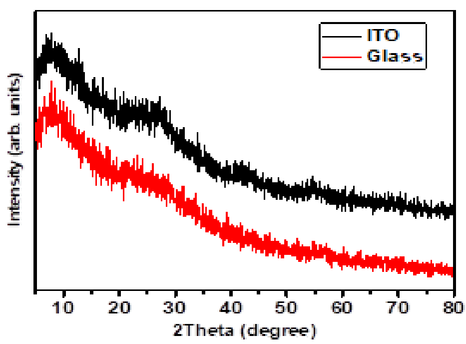

Fig. 5. XRD pattern on the prepared samples in the presence of ITO and glass.

3.3. Optical Properties

The multilayer anti-reflection coating was designed using the Macleod software and optimized through multiple stages using the Simplex method [21]. This software optimizes the thicknesses of layers to achieve optimal transmission, reflection, and absorption properties. In this design, MgF_2 and SiO_2 were chosen as anti-reflection coating and Glass was chosen as the substrate. The optical transmission spectrum of raw glass and ITO substrates is shown in Figure 6. The results show that the maximum optical transmittance of the glass substrate is about 95% and the maximum optical transmittance of the ITO substrate is about 94%. Figure 7 (a) shows the theoretical and experimental optical transmission spectrum in the range of 200 to 1000 nm. The theoretical and experimental graphs reveal that with the deposition of the MgF_2 and SiO_2 anti-reflection coating, the maximum transmission reaches 99%, demonstrating a strong correlation between the theoretical and experimental results. Korkmaz et al. analyzed the incident and transmission spectra of the MgF_2 thin-film created using the Thermionic Vacuum Arc (TVA) method [22]. They showed that the MgF_2 reflection was significantly low. Optical transmission through samples coated with MgF_2 was higher than those without coating.

The bandgap of thin layers can be analyzed using the absorption coefficient (α) through the Tauc equation [23-25].

$$\alpha h\nu = A(h\nu - E_g)^m \qquad (2)$$

Where A is a constant dependent on the effective masses of electron and hole, and material refractive index, h is the Planck's constant, and m equals 2 for direct transition and corresponds to 0.5 for indirect transition materials [26]. Fig. 7 demonstrates the graph of $(\alpha h\upsilon)^2$ against photon energy (hυ) for all the samples. The band gap energy (E_g) values, obtained by extrapolating the linear portion of the curves to x axis ($\alpha h\nu = 0$) [27, 28]. The results of spectroscopy and bandgap showed that the ITO substrate can affect the bandgap and reduce the bandgap. By changing the substrate from glass to ITO, the band gap decreases from 3.89 to 3.27 eV.

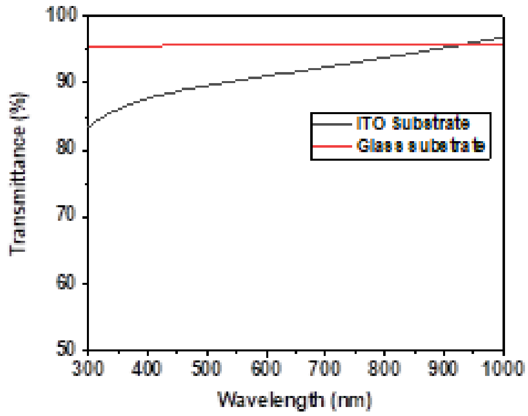

Fig. 6. The optical transmission spectrum of raw glass and ITO substrates.

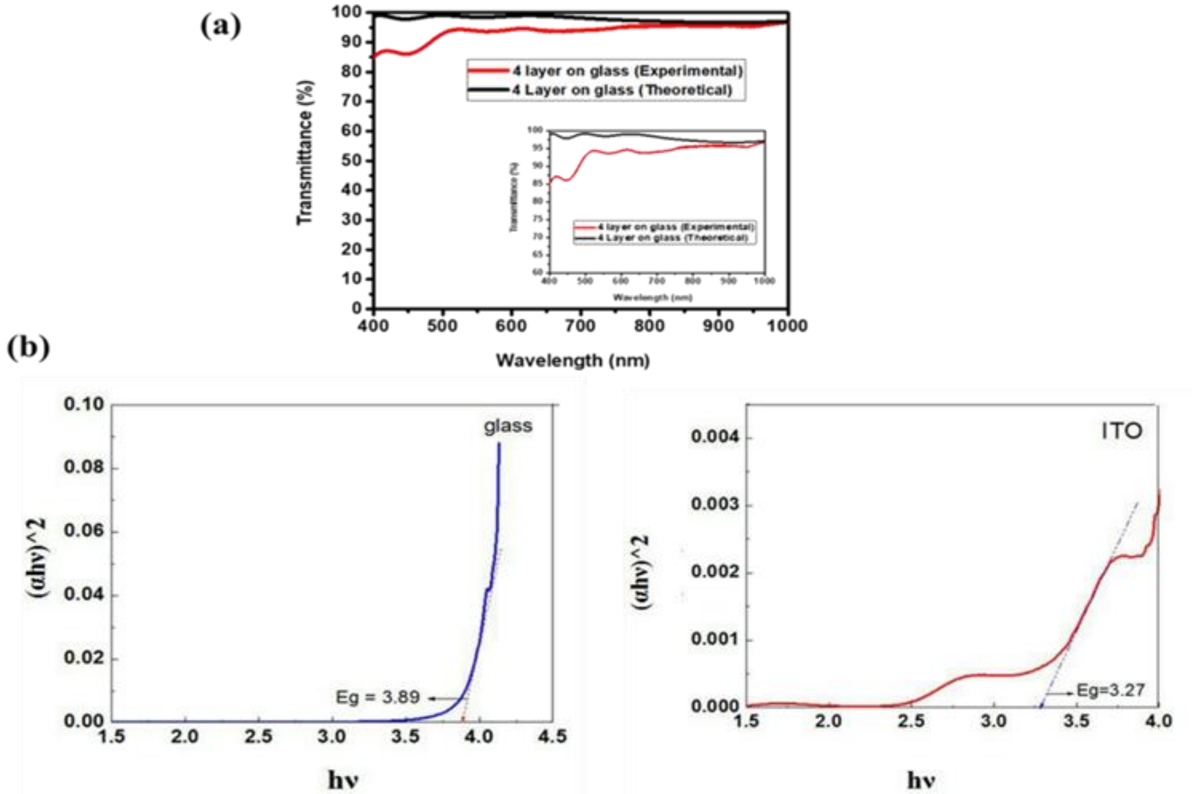

Fig. 7. (a) Theoretical and experimental transmission graphs (b) Plots of $(\alpha h\nu)^2$vs. photon energy (hν) for ITO and glass samples.

4. Conclusion

In this research, MgF_2 and SiO_2 were deposited on different substrates (ITO and glass) through the RF magnetron sputtering method to create an anti-reflective coating. The results of FESEM analysis showed that four layers have grown uniformly. Also, the image of the sample surface showed that the surface of the samples is smooth and their roughness is low. X-ray diffraction results showed that the samples were amorphous. Additionally, evaluating the optical properties of the samples showed that optical transmission reached more than 99 percent, and the bandgap was reduced when ITO was used as a substrate.

Therefore, the utilization of these materials to create anti-reflective coatings and solar panels can be highly effective.

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Conflicts of Interest

The author declares that there is no conflict of interest regarding the publication of this article.

References

[1] Xu, Y., Peng, C., Xin, C. and Wu, J., 2013. Preparation of silica antireflective films for solar energy application. *Materials Letters*, *94*, pp.89-91.

[2] Chen, D., 2001. Anti-reflection (AR) coatings made by sol–gel processes: a review. *Solar Energy Materials and Solar Cells*, *68*(3-4), pp.313-336.

[3] Moayedfar, M. and Assadi, M.K., 2018. Various types of anti-reflective coatings (ARCS) based on the layer composition and surface topography: a review. *Reviews on Advanced Materials Science*, *53*(2), pp.187-205.

[4] Macleod, H.A., 2001. Thin-Film Optical Filters (3rd) Florida.

[5] Zhan, F., Li, Z., Shen, X., He, H. and Zeng, J., 2014. Design multilayer antireflection coatings for terrestrial solar cells. *The Scientific World Journal*, *2014*.

[6] Kaminski, P.M., Lisco, F. and Walls, J.M., 2013. Multilayer broadband antireflective coatings for more efficient thin film CdTe solar cells. *IEEE Journal of Photovoltaics*, *4*(1), pp.452-456.

[7] Lien, S.Y., Wuu, D.S., Yeh, W.C. and Liu, J.C., 2006. Tri-layer antireflection coatings (SiO_2/SiO_2–TiO_2/TiO_2) for silicon solar cells using a sol–gel technique. *Solar Energy Materials and Solar Cells*, *90*(16), pp.2710-2719.

[8] Du, X., Xing, Y., Zhou, M., Li, X., Huang, H., Meng, X.M., Wen, Y. and Zhang, X., 2018. Broadband antireflective superhydrophilic antifogging nano-coatings based on three-layer system. *Microporous and Mesoporous Materials*, *255*, pp.84-93.

[9Kuhr, M., Bauer, S., Rothhaar, U. and Wolff, D., 2003. Coatings on plastics with the PICVD technology. *Thin Solid Films*, *442*(1-2), pp.107-116.

[10] Romach, M.M., Scherer, G., Eichenberger, J., Lanzafame, J., Glocker, D., Jaszcar, M. and Rayner, B., 2014. Inverted cylindrical magnetron sputtering of optical coatings. *2014 Proceedings of the Society of Vacuum Coaters*, pp.233-238.

[11] Hillie, K.T. and Swart, H.C., 2007. Effects of SnO_2 surface coating on the degradation of ZnS thin film phosphor. *Applied surface science*, *253*(20), pp.8513-8516.

[12] DeNatale, J.F., Hood, P.J., Flintoff, J.F. and Harker, A.B., 1992. Fabrication and characterization of diamond moth eye antireflective surfaces on Ge. *Journal of Applied Physics*, *71*(3), pp.1388-1393.

[13] Brinker, C.J. and Scherer, G.W., 2013. *Sol-gel science: the physics and chemistry of sol-gel processing*. Academic press.

[14] Gunasekaran, M., Gopalakrishnan, R. and Ramasamy, P., 2004. Deposition of ZnS thin films by photochemical deposition technique. *Materials Letters*, *58*(1-2), pp.67-70.

[15] Fathy, N., Kobayashi, R. and Ichimura, M., 2004. Preparation of ZnS thin films by the pulsed electrochemical deposition. *Materials Science and Engineering: B*, *107*(3), pp.271-276.

[16] Wang, S., Fu, X., Xia, G., Wang, J., Shao, J. and Fan, Z., 2006. Structure and optical properties of ZnS thin films grown by glancing angle deposition. *Applied surface science*, *252*(24), pp.8734-8737.

[17] Liu, X. and He, J., 2009. One-step hydrothermal creation of hierarchical microstructures toward superhydrophilic and superhydrophobic surfaces. *Langmuir*, *25*(19), pp.11822-11826.

[18] Chen, C.C., Lin, D.J., Don, T.M., Huang, F.H. and Cheng, L.P., 2008. Preparation of organic–inorganic nano-composites for antireflection coatings. *Journal of Non-Crystalline Solids*, *354*(32), pp.3828-3835.

[19] Moghadam, R.Z., Dizagi, H.R., Agren, H. and Ehsani, M.H., 2023. Understanding the effect of Mn^{2+} on Yb^{3+}/Er^{3+} co-doped $NaYF_4$ upconversion and obtaining the optimal combination of these tridoping. *Scientific Reports*, *13*(1), p.17556.

[20] Zarei Moghadam R., Taherkhani M., 2022. Oxygen and nitrogen doped diamond-like carbon thin films: A comparative study, *Progress in Physics of Applied Materials*, 2(2), pp.139-146.

[21] Harris, D.C., 1999. *Materials for infrared windows and domes: properties and performance* (Vol. 158). SPIE press.

[22] Korkmaz, Ş., Elmas, S., Ekem, N., Pat, S. and Balbağ, M.Z., 2012. Deposition of MgF_2 thin films for antireflection coating by using thermionic vacuum arc (TVA). *Optics Communications*, *285*(9), pp.2373-2376.

[23] Gholizadeh, M., Moghadam, R.Z., Mohammadi, A.A., Ehsani, M.H. and Dizaji, H.R., 2020. Design and fabrication of MgF_2 single-layer antireflection coating by glancing angle deposition. *Materials Research Innovations*, *24*(7), pp.442-446.

[24] Moghadam, R.Z., Ehsani, M.H., Dizaji, H.R. and Sazideh, M.R., 2018. Thickness Dependence of Structural and Optical Properties of CdTe Films. *Iranian Journal of Materials Science & Engineering*, *15*(3).

[25] Ashrafi, M.M.A., Dizaji, H.R., Ehsani, M.H. and Moghadam, R.Z., 2018. ZnS Film properties modification using oblique angle deposition technique. *Surface Review and Letters*, *25*(06), p.1850119.

[26] Senthamilselvi, V., Ravichandran, K. and Saravanakumar, K., 2013. Influence of immersion cycles on the stoichiometry of CdS films deposited by SILAR technique. *Journal of Physics and Chemistry of Solids*, *74*(1), pp.65-69.

[27] Chen, F., Cao, Y., Jia, D. and Niu, X., 2013. Facile synthesis of CdS nanoparticles photocatalyst with high performance. *Ceramics International*, *39*(2), pp.1511-1517.

[28] Zarei Moghadam, R., Omrany, A.H., Taherkhani, M. and Shokrian, F., 2021. Fabrication of multi-layer antireflection coating consisting of ZnS and MgF_2. *Progress in Physics of Applied Materials*, *1*(1), pp.7-13.