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Synthesis and Characterization of MgF_2/Cu Coating on Aluminum Produced by Sputtering Technique

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KEYWORDS

Anti-reflectance;
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Physical vapor deposition layer.

ABSTRACT

Anti-reflective (AR) coatings that reduce surface reflectance have attracted more attention in a variety of applications. In this work, the structural and optical properties of MgF_2/Cu bilayer film as an AR coating on an aluminum substrate deposited by sputtering were investigated. The structural and morphological properties were studied by X-ray diffraction (XRD) and field emission scanning electron microscopy (FESEM) respectively. The XRD patterns showed that the coating is composed of pure and crystalline phases. The FESEM and map images show a smooth coating with a uniform distribution of elements. The optical properties of the coating have been investigated by studying the reflectance spectra of the coating. The coverage showed the lowest reflection at high wavelengths. The adhesion strength of the films on the aluminum substrate was determined by a cross-cut test, which obtained a value of 5B for each coating, which indicates the excellent strength of the coatings.

1. Introduction

Today, anti-reflective bandwidth coatings have received a great deal of attention in various fields due to their reduction in surface reflectance, which dramatically reduces unwanted reflectance losses and improves the transmission required over a wide range of wavelengths. These coatings are used in building glass, computer screens, military equipment, photovoltaic cells, solar collectors, light emitting diodes, architectural glass, pneumatic screens, and high-power laser systems [1-3].

Recently, a large number of anti-reflective coatings have been used, such as TiO_2, SiC, SiO_2, Al_2O_3, SiO, ZnO, CaF_2, ZnSe, SiO_2-TiO_2, ZnS, a-SiNx, Ta_2O_5 and Si_3N_4 [2,4]. Among them, magnesium difluoride (MgF_2) has received more attention due to its high permeability and low refractive index ($n \approx 1.38$) in the range of 0.3-0.7 µm and also high chemical and mechanical durability [5]. New research has used two-layer and multi-layer RC coatings. Syed et al. [4] developed TiO_2/MgF_2 multilayer coating by electron beam and resistive thermal evaporation techniques for use in optoelectronic devices. Lee et al. [6] coated MgF_2 and CeO_2 bilayers on crystalline silicon substrates. Sun et al. [2] produced an MgF_2/SiO_2 coating by sol-gel method combined with electron beam evaporation. Ding et al. [7] investigated the synthesis of MgF_2/ZnS dual coatings for use in solar cells.

So far, various methods have been used to fabricate these coatings, such as ion reaction etching, electron beam evaporation, magnetron spraying, plasma chemical vapor deposition (PECVD), atomic layer deposition (ALD), ion-assisted deposition (IAD), ion-beam sputtering (IBS) and the TB process, gel with the layer-by-layer process, spin coating, immersion coating or spray coating [1,2,8].

Meanwhile, the presence of noble metal nanoparticles (Au, Ag, Cu, and Al) due to the efficient excitation of localized surface plasmon resonance (LSPR) oscillation with the light source, provides an efficient medium to improve the anti-reflectance performance [9,10]. When the photon frequency is close to or equal to the oscillation frequency of the electrons around the surface of nanoparticles, it is simply seen as a photon that is rapidly absorbed by the free electrons in the nanoparticles to the surface of the small nanoparticles, intensifying the electric field around the surface of nanoparticles [11,12].

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Plasmonic metasurfaces are very attractive materials because the absorbed wavelengths can be fine-tuned by adjusting their geometric structure. They are also highly sensitive to changes in refractive index in the environment, which opens up a potential way for adjustment [11, 13]. So far, silver [10, 14], gold [15, 16], and other metals have been used to improve the anti-reflectivity of MgF_2, but the effect of copper has not yet been investigated.

Because MgF_2 molecules evaporate directly without decomposition, its thin film can be prepared by conventional thermal evaporation methods such as physical vapor deposition (PVD). It is observed that the optical properties of RC coatings depend on the deposition conditions, deposition techniques, coating material, and the number of coating layers. In this research, MgF_2/Cu anti-reflective coating on the aluminum substrate for use in military equipment and aerospace is produced by the PVD method and evaluated.

2. Methodology

In this study, coating by physical vapor deposition (PVD) method and with thermal evaporation devices by DC method (made by Sharif University Jihad, EDS model) and magnetic sputtering with DC and RF sources (made by Yarnikan Saleh, MSS model) in vacuum conditions were performed on the aluminum substrate. The coating process was started with a base pressure of 6-10 mbar after a pumping time of 2 h. Prior to the process, the substrates were cleaned once for 15 min and once for 5 min with acetone in an ultrasonic device. A molybdenum plant with a melting temperature of 2623 °C was used to evaporate the raw materials.

Two types of coatings were prepared on aluminum 5181 (2.2-2.8% Mg, 0.45% max Si, 0.15-0.35% Cr, etc.) plates as substrate: 1) MgF_2 coating with a thickness of 300 nm, and 2) Coating of two layers of copper and MgF_2 with a thickness of 150 nm each. Magnesium fluoride powder (with a purity of 99.99%) and copper powder were used as raw materials to create coatings.

2.1. Characterization

To identify the phases in the samples, an X-ray diffraction device (Bruker model D8 Advance, Germany) with copper anode and wavelength (CuKa) 540566Å, current 30 mA, voltage 40 kV was used. Determination of chemical composition and molecular structure in coatings made by infrared spectroscopy (FTIR) analysis in the frequency range of 400-4000 cm-1 was performed by ABB-Bomem model MB-100.

The microstructure and morphology of the coating surface were investigated by field emission scanning electron microscopy (FESEM) equipped with EDS analysis (MIRA3 TESCAN model, Czech Republic). Reflection spectra were measured by a spectrometer (Perkin-Elmer Lambda 750, USA) equipped with an integrating sphere. Surface adhesion between the coating and the aluminum substrate was measured according to ASTM-D3359.

3. Results and Discussion

Figure 1 shows the XRD spectrum of a sample with MgF_2 and MgF_2/Cu coatings. The MgF_2 coating spectrum shows purely MgF_2 peaks (consistent with JCPDS no. 41-1443). The XRD spectrum with peaks at angles of 27.2, 35.3, 40.3, 43.8, etc., which belong to planes (110), (101), (200), (111), etc., respectively, confirms the crystal structure and shows the tetragonal crystal structure (tetragonal P42/mnm phase) [17]. In a study, De et al. [18] created a thin film of MgF_2 with a non-conventional magnetron sputtering. The coating had an amorphous structure. They stated that the reason for the amorphous structure was the shorter distance from the target to the bed in this coating technique due to the better surface mobility of the atoms. Zhao-Qi et al. [19] applied Ag-MgF_2 cermet films by vacuum vapor deposition method. They succeeded in producing films consisting mainly of an amorphous MgF_2 matrix with embedded crystalline silver particles.

In pattern 1b, in addition to MgF_2 peaks, there are also Cu peaks (JCPDS no. 04-0836). The peaks at angles 43.3, 50.5, and 74.2 correspond to planes (111), (200), and (220) in the crystalline structure of copper, respectively. This figure shows the purity of the chemical composition of the coatings.

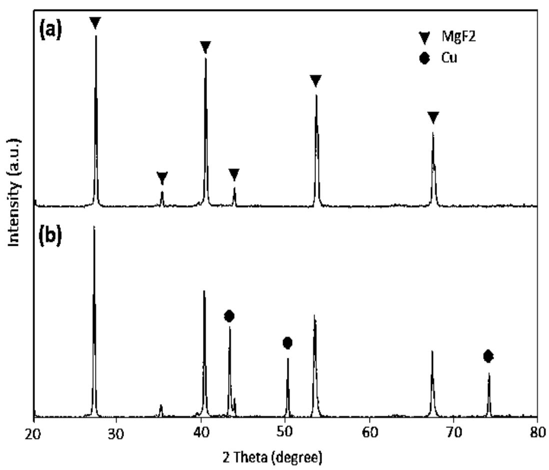

Fig. 1. XRD pattern of synthesized coatings, a) MgF_2 and b) MgF_2/Cu

Figure 2 shows the FTIR spectra of the produced MgF_2 and MgF_2/Cu coatings. Extensive adsorption at 400 to 500 cm^{-1} is due to the combination of Mg-F and Cu-Cu tensile vibrations. Strong adsorption peaks in the regions of about 3448 cm^{-1} and 1651 cm^{-1} are characteristic of H-O-H bending (H_2O molecules) and indicate the presence of hydroxyl groups in the coating [20, 21].

Figure 3 shows the FESEM image of the surface of the synthesized coatings.

Figures 4 and 5 also show the distribution of elements on the coating surface. SEM images clearly show that evaporated and altered sputtered films have good surface quality. In the MgF_2 coating, the Mg and F elements are evenly distributed on the Al substrate. In the MgF_2/Cu coating, in addition to the Mg and F elements, the Cu element in the coating also had a uniform distribution. Weimer et al. [5] produced an MgF_2/Al multilayer thin film by a vacuum deposition chamber. The results showed that the MgF_2 layers contained magnesium vacancy and that F was located at the MgF_2/Al boundary, which may form AlF_3. In the present study, no other compounds were identified except MgF_2 and Cu. The sedimentation method has a significant effect on the optical and microstructural properties of MgF_2 film. Also, the results show that the deposition parameters of sputtered MgF_2 films can be easily controlled to produce the desired layer.

MgF_2 thin films produced by the thermionic vacuum arc technique are smooth, rough, homogeneous, and adhesive. This technique is suitable for producing single-layer and multi-layer anti-reflective coatings [1]. The thickness of the synthesized coatings is shown in Fig. 6. As can be seen, both coatings created by the PVD method have a thickness of about 300 nm.

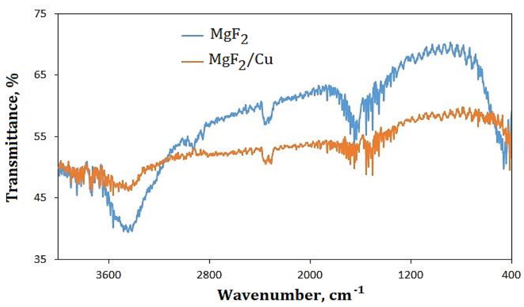

Fig. 2. FTIR pattern of synthesized coatings (MgF_2 and MgF_2/Cu)

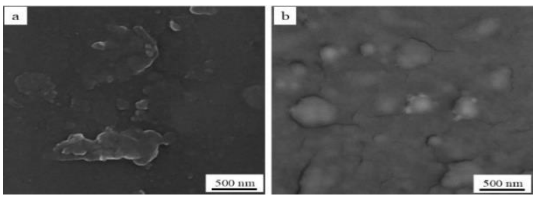

Fig. 3. FESEM image of the surface of the synthesized coatings, (a) MgF2 and (b) MgF2/Cu

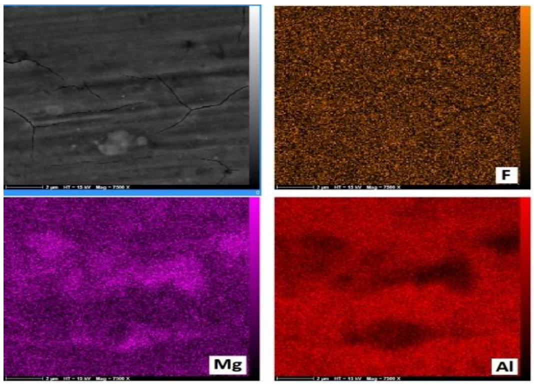

Fig. 4. Map image of MgF_2 coating surface

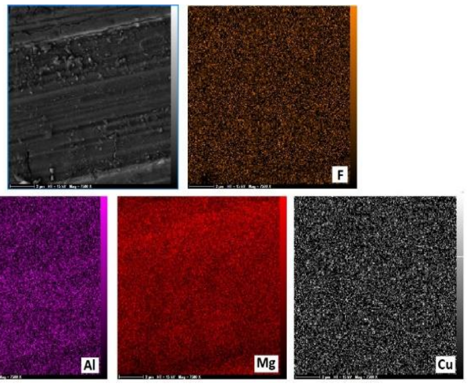

Fig. 5. Map image of MgF2/Cu coating surface

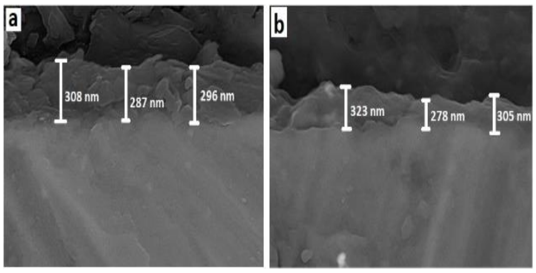

Fig. 6. The thickness of the produced coatings, (a) MgF_2 and (b) MgF_2/Cu

Figure 7 shows the reflection of synthesized coatings MgF_2 and MgF_2/Cu relative to the aluminum substrate as a function of wavelength. The highest reflectance for both samples at 368 and 431 nm was obtained for MgF_2 and MgF_2/Cu, respectively. Usually, the optical spectra obtained for the sample produced by the evaporation method are in good agreement with the theory. With the addition of copper coating, a relatively broad resonance structure occurs following an increase in the intensity, width, and maximum integral wavelength [22]. However, the layer obtained from the sputtering method shows a different behavior compared to the theory. Increased film absorption as a result of disassociating MgF_2 has been reported by Coleman [5].

Extinction coefficient data have also shown that ion-beam sputtered MgF_2 is a good candidate for protecting Al films from a high reflection of at least 121.6 nm [23]. Similar observations were made by Martino et al. [24], who deposited samples of MgF_2 sputtering in the granular form under the Ar atmosphere. They attributed the high absorption with increasing power to the increased dissociation of the target compound at high power, which led to a lack of fluoride in the samples [23].

Korkmaz et al. [1] investigated the transmittance spectra and reflectance of MgF_2 thin film produced by the thermionic vacuum arc (TVA) technique. They showed that the MgF_2 reflection was very low as expected. The transmittance of samples coated with MgF_2 was higher than samples without coating. Zhao-Qi et al. [19], by investigating the Ag-MgF_2 coating synthesized by vacuum evaporation in the visible UV region of 200-800 nm, showed that the cermet film has very low reflectivity and very strong absorption for light waves of 220-800 nm. Its absorption was higher than 85% and its reflection was about 51%.

In order to evaluate the adhesion strength of the coating to the substrate surface, a cross-cut adhesion test was performed. This method is proposed as a standard method for quantifying the adhesion of protective coatings on the substrate and is classified as grades 5B, 4B, 3B, 2B, 1B, and 0B from the highest (5B) to the poorest (0B) adhesion, respectively. Figure 8 shows the adhesion test image of the coatings. The adhesion strength of both coatings MgF_2 and MgF_2/Cu was 5B.

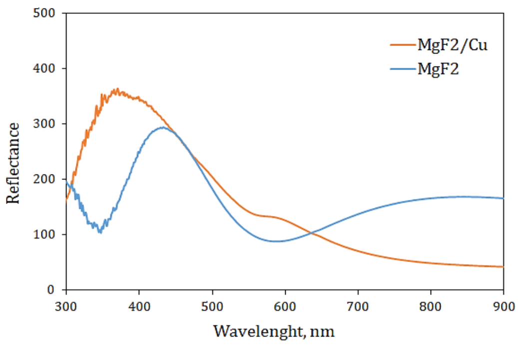

Fig. 7. Reflection spectra of synthesized MgF_2 and MgF_2/Cu coatings

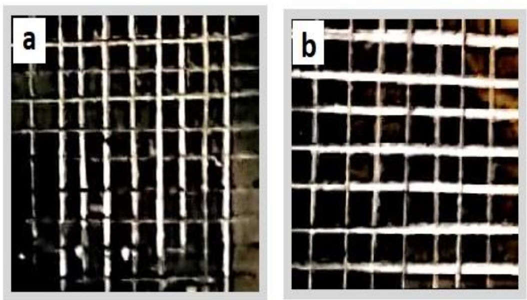

Fig. 8. Cross-cut test image to determine adhesion between coatings and substrate surface, (a) MgF_2 coating and (b) MgF_2/Cu coating

4. Conclusions

In this work, MgF_2/Cu coating was successfully created on the aluminum substrate by physical vapor deposition (sputtering). Analysis of the results showed that a coating with a thickness of 300 nm containing pure crystalline phases was formed. Uniform distribution of elements in coatings and good adhesion to the substrate was observed. Investigation of the reflectance spectrum of MgF_2/Cu coating showed that copper reduces the light reflection in the visible light range due to the localized surface plasmon resonance. Therefore, this coating was used in anti-reflection applications.

Conflicts of Interest

No potential conflict of interest was reported by the authors.

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