Optical properties of ZnO/MgF$_2$ bilayer thin films prepared by PVD technique

Malek A.H. Muhi

Nanotechnology and Advanced Materials Research Center, University of Technology, Baghdad, Iraq
E-mail: malik_muhi@yahoo.com

Abstract
Zinc Oxide (ZnO) is considered as one of the best materials already used as a window layer in solar cells due to its antireflective capability. The ZnO/MgF$_2$ bilayer thin film is more efficient as antireflective coating. In this work, ZnO and ZnO/MgF$_2$ thin films were deposited on glass substrate using pulsed laser deposition and thermal evaporation deposition methods. The optical measurements indicated that ZnO thin layer has an energy gap of (3.02 eV) while ZnO/MgF$_2$ bilayer gives rise to an increase in the energy gap. ZnO/MgF$_2$ bilayer shows a high energy gap (3.77 eV) with low reflectance (1.1-10%) and refractive index (1.9) leading to high transmittance, this bilayer could be a good candidate optical material to improve the performance of solar cell window.

Key words
Antireflection coating, thin film, ZnO, MgF$_2$.

Introduction
During the recent past years, antireflective coatings (ARC) of various materials have attracted increasing attention as a great importance to get low reflectance solar cell. Various coatings such as ZnS, MgF$_2$, ZnO have been used in this application. The importance of antireflective coating comes during in solar cell fabrication process which adds a significant improvement in solar cell efficiency [1, 2]. Zinc oxide (ZnO) is a metal oxide of the II–VI compound semiconductor group with n-type conductivity and has band gap energy...
of 3.37 eV for bulk material at room temperature; the high band gap of ZnO makes it transparent to visible light [3]. Due to the significant properties ZnO is a promising compound for electronic or optoelectronic such as solar cells (anti-reflecting coating and transparent conducting oxides), gas sensors, liquid crystal displays, heat mirrors, surface acoustic wave devices etc [4-6].

In the present work, ZnO and MgF₂ have been chosen to prepare a bilayer antireflective coating. ZnO/MgF₂ bilayer antireflection coating has been investigated because monolayer antireflective coating is not suitable to cover a broad range of the solar spectrum. One of the basic principles indicates that materials with higher refractive index are preferred for the bottom layer while lower refractive index for the upper-layer of a double-layer antireflection coating [7]. Furthermore, the single-layer antireflective coating is achieved lowest reflection for a single wavelength of incident radiation; it must retain [8]:

(a) Square root of the refractive indices of the materials constrained the coating equal to the refractive index of the ARC.
(b) Optical thickness of ARC equal to one quarter of the wavelength.

Therefore, the single layer antireflective coating able to be non-reflective only at single wavelength, it is normally at the middle of the visible spectrum. This problem has solved by using the double layer antireflective coating to cover over the whole visible spectrum are more effective.

**Experimental part**

Bilayer thin film has been deposited by Physical Vapor Deposition (PVD) method, resistor heating thermal evaporation system has been used to deposit MgF₂ layer and pulsed laser deposition system has been used to deposit ZnO thin layer. Both systems were under high vacuum by rotary and diffusion pumps, Penning and Pirani gauges were used to monitor vacuum in these systems.

Glass slides were used as a substrate for thin films. Before deposition, the substrates were cleaned by deionized water and ethanol. Then, these substrates were dried for about 10 minutes. Both powders ZnO and MgF₂ with the purity approximately 99.999 % were used as sources materials.

The preparation of thin film was divided in two sections:
First layer: ZnO thin films were grown on glass slide substrates using a pulsed laser deposition technique. This film was deposited in vacuum environment about of 1×10⁻⁵ mbar. The Q-switched Nd:YAG laser was used to deposit with the parameters of laser as number of pulses 200 pulses, wavelength \( \lambda = 1064 \, \text{nm} \), energy 700 mJ, repetition rate of 2 Hz and the pulse duration \( \approx 8 \, \text{ns} \). Furthermore, the distance between the substrates and the target plate was 30 mm, and the substrates heat was maintained at 400 °C within deposition process.
Second layer: MgF₂ was grown as second layer on ZnO thin film using thermal evaporation technique. Under high vacuum, MgF₂ powder was heated to reach temperature greater than the melting point of this powder by applying current on ends of tungsten boat which was 180 mm away from substrates.

The optical properties of the thin films such as reflectance, transmittance, energy band gap and refractive index were calculated. The transmittance was measured by Metertech Inc. SP-8001 UV-VIS Spectrophotometer in UV–VIS wavelengths ranged from 300 to 1100 nm. The reflectance was measured using Avalight-DH-S-BAL diffused
reflectance spectrometer in UV–VIS wavelengths ranged from 250 to 900 nm.

**Results and discussion**

The optical properties for ZnO thin film and ZnO/MgF$_2$ thin film deposited on glass substrates were analyzed, the reflectance, absorbance and transmittance have been studied. Additional, The optical energy gap and optical constants have been calculated. Fig.1 shows the reflectance measurements in the range of wavelengths 250–900 nm, both films have lowest reflectance in ultraviolet region. In general, it will be seen that all figures of the optical properties for both tested thin films have the same behavior themselves carves in range 640-1100 nm. However, there are noticed constant different values in y-axis.

In Fig. 1, reflection spectrum of ZnO film shows the minimum reflection of 3 % at 308 nm while reflection spectrum of ZnO/MgF$_2$ coating shows the minimum reflection of 1.1 % at 301 nm within the wide range of wavelengths (250-900) nm. In additional, the ZnO/MgF$_2$ reflectance is 10 % within the visible wavelength range. However, there is clear reduction in reflectivity by depositing a second layer.

![Reflectance of ZnO and ZnO/MgF$_2$ thin films.](image)

The results of transmission spectrum were consistent with the results of reflectivity, as shown in Fig. 2. The spectrum of ZnO/MgF$_2$ coating film is no drop of the total transmittance in the any reign of wavelength range (350-1100) nm but the spectrum of ZnO coating is gradual slope drop in visible wavelength toward ultraviolet. The transmittance spectrum of ZnO/MgF$_2$ coating in the all wavelength region $\lambda$= (350-1100) nm is greater than (85%). This average value of transmittance is acceptable comparing with others [9], and it may be due to depend mainly on three factors [9], i.e., (1) oxygen deficiency; because thin film was
deposited by pulsed-laser deposition with poor transparencies. (2) surface roughness; scattering ray from surface must be reduction the transmission depending on the grain size, and (3) impurity centers. In this work, the loss of light in ZnO thin film is mainly due to the surface roughness and the oxygen vacancies.

The optical band gaps of the both films were evaluated from Eq. (1) [10]:

\[ (\alpha h\nu) = A(h\nu - E_g)^m \]  \hspace{1cm} (1)

where \( \alpha \) is the absorption coefficient, \( A \) is proportionality constant and \( E_g \) is optical energy band gap. \( m \) equal to \( \frac{1}{2} \) for direct band gap material. The absorption coefficient was calculated using the following expression [10, 11]:

\[ \alpha = \frac{1}{t} \ln(T) \]  \hspace{1cm} (2)

where \( t \) is the thickness of the film and \( T \) is the transmittance.

The plot \((\alpha h\nu)^2 \) versus the photon energy \((h\nu)\) were evaluated the direct band gap \((E_g)\) of the ZnO/MgF$_2$ and ZnO thin films which were found to be 3.77 eV and 3.05 eV respectively as shown in Fig. 3. This result, of ZnO thin film, is good agreement with previously reported data of ZnO thin film [12, 13].
Fig. 3: Energy band gap of ZnO and ZnO/MgF$_2$ thin films.

Fig. 4 shows the refractive index of both Films, and the films have high refractive index (2.5) and (1.95) at wavelength (350 nm) for ZnO and ZnO/MgF$_2$ receptively. The refractive indexes of the both films were evaluated from Eq. (3) [14]:

$$k = \frac{a\lambda}{4\pi}$$  \hspace{1cm} (4)

where, R is the reflectance of the film and $\lambda$ is the wavelength of the incident beam. then the both values decrease to meet them at wavelength 640 nm and reach a value (1.9).

Fig. 4: Refractive index as a function of wavelength for ZnO and ZnO/MgF$_2$ thin films.
The relationship between absorption coefficient $\alpha$ (cm$^{-1}$) and wavelength shows in Fig. 5. It is noticed that absorption coefficient for ZnO/MgF$_2$ thin film has nearly constant with wide range wavelength while absorption coefficient of the ZnO thin film is decrease with increase wavelength. Also it can be noticed the value of absorption coefficient for bilayer thin film is approximately ($10^4$ cm$^{-1}$). This may be related to decrease in grain size which causes the light scattering effect for its low surface roughness [15]. This may be explained as the variation of the carrier concentration with respect to the ion-implanted concentration and the increase of the ionized impurity scattering.

![Absorption Coefficient](image)

**Fig. 5: Absorption confident as a function of wavelength for ZnO and ZnO/MgF$_2$ thin films.**

Fig. 6 shows the extinction coefficient ($K_0$) as a function of wavelength for two thin films which they were determined from transmitted spectra. The extinction coefficient of ZnO thin film is decrease as the wavelength increases while the bilayer thin film is increases as the wavelength decrease, which is consistent with other reports [16].

![Extinction Coefficient](image)

**Fig. 6: Extinction coefficient as a function of wavelength for ZnO and ZnO/MgF$_2$ thin films.**
Conclusions

ZnO and ZnO/MgF$_2$ thin films were successfully deposited into glass substrate using pulsed laser deposition and thermal evaporation deposition as window in solar cell application due to its low reflectance. Present ZnO has low energy gap (3.02 eV) while ZnO/MgF$_2$ results in an increase of the energy gap. The most promising ZnO/MgF$_2$ showing the highest energy gap (3.77 eV) with low reflectance (1.1-10%) and refractive index (1.9) leading to high transmittance which is very promising optical material to improve the performance of solar cell window.

Acknowledgement

The author is gratefully acknowledged Nanotechnology and Advanced Materials Research Centre, University of Technology, Baghdad, Iraq for conducting all tests. Also he is very thankful to Miss Alaa Adnan Rashad, Department of Chemistry, College of Science, Al-Nahrain University for measuring reflectance optical test. He is many thank to Ms. Zeina Yassin Abbas, Nanotechnology and Advanced Materials Research Centre, University of Technology, Baghdad for measuring UV-Vis spectrophotometer test.

References

[1] M.-L. Kuo, D. J. Poxson, Y. S. Kim, F. W. Mont, J. K. Kim, E. F. Schubert, S.-Y. Lin, Opt. Lett., 33, 21 (2008) 2527-2529
[2] M. Nam, J. Lee, K.-K. Lee, Microelectron. Eng., 88 (2011) 2314-2318.
[3] K. R. Gbashi, A. T. Salih, A. A. Najim, M. A. Muhi, J. of Materials Science: Materials in Electronics, 20 (2017) 1-6.
[4] K. L. Chopra, S. Major, D. K. Pandya, Thin Solid Films, 102, 1 (1983) 1-46.
[5] S. Bose, A. K. Barua, J. of Physics D: Applied Physics, 32, 3 (1999) 213-218.
[6] H. Kim, C. M. Gilmore, Applied Physics Letters, 76, 3 (2000) 259-262.
[7] S. E. Lee, S. W. Choi and J. Yi, Thin Solid Films, 376, 1-2, 1 (2000) 208-213.
[8] K. Ali, S. A. Khan, M. Z. Mat Jafri, Int. J. Electrochem. Sci., 9 (2014) 7865-7874.
[9] Vinay Gupta and Abhai Mansingh, J. of Applied Physics, 80, 2 (1996) 1063-1074.
[10] Ammar T. Salih, Aus A. Najim, Malek A.H. Muhi and Kadhim R. Gbashi, Optics Communications, 388 (2017) 84-89.
[11] A. A. Najim, M. A. Muhi, K. R. Gbashi, A. T. Salih, Plasmonics, (2017) 1-5.
[12] K. Yoshino, T. Fukushima, M. Yoneta, J. of Mater. Sci.: Mater. in Electronics, 16, 7 (2005) 403-408.
[13] A. Zaier, A. Meftah, A.Y. Jaber, A.A. Abdelaziz, M.S. Aida, Journal of King Saud University-Science, 27 (2015) 356-360.
[14] V. Gowthami, M. Meenakshi, P. Perumal, R. Sivakumar, C. Sanjeeviraja, International J. of ChemTech Research, 6, 13 (2014) 5196-5202.
[15] Adawiya J. Haidar & Gehan E.Simon, Engineering & Technology J., 27, 14 (2009) 2653-2665.
[16] Sodky Hamed Mohamed, Philosophical Magazine, 91, 27 (2011) 3598-3612.