STUDIES ON MAGNETRON SPUTTERED TIO_2/ZNO BI-LAYER HEAT REFLECTOR COATING

Rajesh Das

Associate Profesor Department of Applied Sciences, Haldia Institute of Technology, Haldia-721657, Purba Medinipur, West Bengal, India.

Abstract : The authors report on the heat reflector properties of ZnO/TiO_2 bi-layer films deposited by rf-magnetron sputtering at 450°C substrate temperature. ZnO/TiO_2 bi-layer film shows 80% visible transmission and 60% infra-red reflection with plasma resonance frequency at 1200nm. Heat reflecting properties of the proposed bi-layer coating is achieved by suitable combination of refractive index and individual film thickness. TiO_2 is highly resistive (resistivity is of the order of 10^{10} ohm-cm), and has 85% visible optical transmission and very low absorption in the visible and infrared regions. The refractive index of TiO_2 film is 2.6 at a substrate temperature 250°C and 2.9 at 450°C. The surface roughness of TiO_2 thin film varied from ~1.94 -14.23 nm and crystallite size is approximately 20 nm. At 450°C, the rutile titanium dioxide structure was formed which was confirmed on the basis of diffraction rings. ZnO thin films show more than 90% visible transmission and refractive index is 1.58. Individual film thicknesses in the bilayer coating were 420nm and 48nm respectively for ZnO and TiO_2 thin film respectively.

Keywords: ZnO/TiO_2 bi-layer thin film; RF-Magnetron sputtering; heat reflection optical coating; Structural properties.

1. Introduction

Thin film coating has wide range of applications such as antiglare and antireflective coatings, conductive, and transparent heat reflector; EMI shielding; polarizers; thin film beam splitter, dichroic, static dissipating and band pass filters; night vision compatibility filters; fine wire meshes; and a wide variety of custom optical enhancements. Transparent coating with infra-red (IR) shielding is strongly desired for many applications such as in automobile windows, aircraft windscreens and ice cream parlours. The requirements are high transmission in the visible range (higher than 80%) for safe driving and IR reflection for shielding against heat waves (wavelength between about 800 and 2600 nm).

Single layer thin films (indium tin oxide, antimony tin oxide, zinc oxide, etc) do not satisfy both requirements [1–4]. Sawada and Taga [5] have developed an improved transparent TiO_2/ITO multi-layer IR reflector in selective wavelength range from 800 to 1200 nm. Multi-layer oxide films, such as TiO_2/SiO_2 and Indium tin oxide (ITO)/silver/ITO multi-layer films, provide a high visible transmittance, coupled with good IR reflectance. ITO and TiO_2 have an interesting combination of refractive indices (n) and extinction coefficients with proper film thickness.

Titanium dioxide (TiO_2) thin films have wide applications due to many excellent chemical, electrical, dielectric and optical properties such as high optical transmittance in visible region, wide band gap, high refractive index, and good chemical stability, which make them suitable for photo-electrodes in solar cells [6], catalytic surfaces for water purification [7-9], antireflection coatings

[10], as protective layer for very large scale integrated (VLSI) circuits etc. The high dielectric constant of TiO_2 allows its consideration as an alternative to silicon dioxide for ultra-thin gate oxide dielectrics used in memory and logic devices. TiO_2 films with high bandgap, excellent visible transmittance alongwith high refractive index values make them suitable for optical coating development.

On the other hand, ZnO is an interesting materials with wide and direct band gap (3.37 eV) II–VI compound semiconductor with large excitonic binding energy 60 meV. Based on its good optical and electrical properties, ZnO has many applications such as a transparent conductive contact, thin-film gas sensor, solar cell, luminescent material, and UV laser [11–15]. All the ZnO films provide excellent UV shielding due to the absorption edge on the short wavelength side (ë<300 nm). The other advantages of ZnO films are their low cost, non-toxicity [11], ease of doping and excellent chemical stability. Multilayer optical coating are developed by several group of researcher for different technological applications [16-18].

The oxide films can be deposited by different methods such as sol–gel, chemical vapor deposition, spray pyrolysis, vacuum evaporation, sputtering and electron beam evaporation. RF-magnetron sputtering is a very efficient method for uniform, damage free films deposition with precise thickness control and high sticking co-efficient over large area. The Optical properties, growth morphology, the crystal structure and the stoichiometry of ZnO and TiO_2 films are very sensitive to the sputtering conditions. RF-power, oxygen partial pressure, and substrate temperature plays a critical role in determining the coating quality in terms optical, structural and morphological properties.

In this paper properties of the ZnO and TiO_2 films deposited under $Ar + O_2$ ambient have been investigated and TiO_2/ZnO bi-layer structure has been fabricated. Significant improvement in IR-reflection of the TiO_2/ZnO bi-layer films has been obtained. The aim of this work is to produce film that will eliminate the infrared portion of the solar spectrum. Here, transmission and reflection, as well as the structural properties, surface texture of individual layers (ZnO and TiO_2) and combined layers have been studied.

2. Experimental Details

Aluminium-doped Zinc Oxide films were deposited by a dual target Radio frequency (RF) magnetron sputtering system (Hind High Vacuum) using a sintered ceramic disc of $ZnO{:}Al_2O_3$ (2wt%) as the target (diameter 2-inches) under $Ar+O_2$ gas ambient with different O_2 concentration (C_o was varied from 2% to 20%) at RF-power 100watt, chamber pressure 4mtorr.

TiO_2 thin films were deposited by a three target Radio frequency (RF) magnetron sputtering system using Ar as sputtering gas and O_2 as reactive gas at substrate temperature $T_s = 450^0C$. The target was hot-pressed sintered TiO_2 ceramic having a purity 99.99%. The substrate was 7059 Corning glass. The rf-power and chamber pressure were varied from 60 to 120W at fixed chamber pressure 5mTorr in order to obtain optimum deposition conditions TiO_2.

Argon flow in the deposition chamber was regulated by a mass flow controller and was fixed at 50 sccm. Before each deposition, the base pressure inside the deposition unit was brought down to 3′10-7Torr Pressure. The gas flow was maintained by mass flow controllers and the chamber pressure was kept constant with the help of a throttle valve. Substrates were placed parallel to the target surface at a distance of 7cm. The substrate temperature was monitored by a thermocouple and varied in the range 350^{0}C-450^{0}C.

The optical transmission and reflection were measured using a UV-VIS-NIR double-beam spectrophotometer (Hitachi, Japan) in the wavelength range 185-2600nm. The standard measurement technique was followed to obtain the transmission and reflection spectra. After initialization of the instrument, the background correction is done. The effect of the glass substrate was eliminated because the measurement was performed on film with glass with respect to a glass substrate. Refractive indices of these films were calculated using Goodman's formula considering interference oscillation. The structural studies were performed by transmission electron microscopy (TEM) and transmission electron diffraction (TED). The surface topography and roughness factor of ZnO, TiO_2 and bi-layer films were studied by AFM.

3. Results and Discussions

ZnO:Al films deposited under Ar+O_2 ambient under optimum condition shows high conductivity and with increase of C_o values resistivity of ZnO films increases. In our case, ZnO: Al thin film prepared under Ar ambient (C_O=0%) shows the minimum resistivity of the order of 10^{-4} ohm-cm in the optimum condition. The resistivity of ZnO:Al films increases with increase of O_2 partial pressure i.e. with increase of C_O values shown in Table-1.

On the other hand TiO_2 films are highly insulating. Both ZnO and TiO_2 are highly transparent over broad spectrum of wavelength.

Fig.1a shows the optical transmission spectra of ZnO:Al films deposited under Ar+O_2 ambient with different oxygen concentration (C_O) in the gas mixture. The average transmittance in the visible range is found to be above 90% for all the films. All the ZnO films provides an excellent UV shielding as the absorption edge in the lower wavelength side is at l= 300nm. From fig.1 it is evident that %transmittance increases in both visible and IR-region with the increase of oxygen concentration ratio. Another important feature has been observed that both transmission (T) and reflection (R) decreases in the near IR-region and the value of reflection thereafter increases. Since doped ZnO is degenerate semiconductor, this behavior can be explained in terms of the classical Drude theory. In the near IR-region, the decrease in both R and T are due to free carrier absorption. The high transmission in the visible range is understood from the fact that ZnO is direct band gap semiconductor with high band gap.

Fig.1b shows the optical transmittance (T) and reflectance (R) of TiO_2 films deposited at 450^{0}C with Ar-flow 50 sccm at different rf-power varying from 50 watt to 100 watt. All TiO_2 films act as insulator but give ~ 85% transmission over wider range of wavelength (250nm to 2600 nm). The spectra show pronounced interference oscillations those are originated from variations of thickness and refractive index of the films. The position and height of the reflectance peak of TiO_2 films have changed and consequently refractive index have also changed with the change of rf-power. With the increase of rf-power transmission minima has shifted towards the infrared region and number of oscillations have been increased.

The index of refraction (n_1) and the film thickness of TiO_2 thin films are calculated using Goodman formula [19] from the interference pattern of the optical transmission spectrum of the transparent films.

$$n_1 = \frac{\left[(1+n_2)+\sqrt{(1+n_2)^2 - 4n_2T_m}\right]}{2\sqrt{T_m}}$$

$$\text{and } d_1 = \frac{\lambda_1\lambda_2}{2(\lambda_1 - \lambda_2)n_1}$$

Where, l-$_1$ and l-$_2$ are the wavelengths for two consecutive interference maxima, T_m is the transmission minimum in between l-$_1$ and l-$_2$; and n_2 is the refractive index of the substrate material. The value of refractive index (r.i) and film thickness of TiO_2 films have been tabulated shown below (Table-2) and maximum r.i value is 2.44. Here, variations of refractive index of TiO_2 thin films are observed for the variation of rf-power.

The refractive index (n) of ZnO thin film is estimated from the interference pattern of ellipsometric data and it varies from 1.4 to 1.8 in the visible wavelength range (shown in Fig.2).

Fig.3 shows AFM images (2D and 3D topography) of ZnO:Al, TiO_2 and TiO_2/ZnO:Al bilayer films respectively. Fig.3a,b shows the textured surface with granular structure of ZnO:Al films deposited under $Ar+O_2$ ambient with $C_O = 2\%$ and the surface roughness is 13.2nm whereas the TiO_2 film is very flat (shown in Fig.3c,d) and its roughness is 1.95nm. But the combined bilayer surface is textured and roughness value in this case is 4.44nm. Fig.4 shows the High Resolution Transmission Electron Micrograph and corresponding electron Diffraction of TiO_2 and ZnO:Al films respectively. From Fig.4a it is evident that TiO_2 film prepared at T_s=450^{0}C and 100watt rf-power, consists of mixture of amorphous and crystalline phase consisting of quite sharp lines and prominent dots are observed from electron diffraction. Here, it is also clear that better crystallinity has been formed along and near the dots. Fig.4b shows the amorphous structure of TiO_2 film prepared at 80watt rf-power but the same film prepared under 60watt shows higher crystallinity shown in Fig.4c. From Fig.4c, it is evident that the film consists of crystalline phase with highly aligned sharp lines in transmission electron micrograph and prominent dots in electron diffraction pattern. It is assumed that the TiO_2 film deposited with 60 watt rf-power have rutile structure. Fig.4d shows the polycrystalline ZnO:Al films with average grain size lying between 10-20nm. Sharp rings correspond (002) and (004) orientations with good crystallinity.

Finally, these two optimized TiO2 and ZnO:Al films are stacked to form the bilayer heat reflective coating. Each film thicknesses in the bilayer stack are 48nm and 420nm for TiO_2 and ZnO film respectively. Fig.5 shows Optical Transmission (%T) and Reflection (%R) of TiO_2/ZnO:Al bilayer film. From the above results it is clear that the ZnO:Al film is more compact, non-stoichiometric, void free and highly crystalline. We know that the ionic radii of Zn^{2+} and Al^{3+} are 72pm and 53pm.In case of Al doped ZnO thin film, segregation of $Al\text{-}^{3+}$ at Zn^{2+} site creates one extra free carrier in the substitution process. At low oxygen partial pressure collision probability of the particles are less as the mean free path of the particles for deposition are longer whereas in the higher gas pressure the particles collide with many other particles arriving at the substrate. With increase of oxygen partial pressure, collision increases and oxygen atom absorption in substrate surface increases. The adsorbed oxygen atoms into the film act as electron traps and decrease the mobility, as a result the resistivity of ZnO:Al film increases. In our case, reactively sputtered (under $Ar+O_2$ ambient) ZnO: Al film were deposited under higher substrate temperature, and as a result the oxygen desorption on the grain boundary of ZnO:Al thin film takes places due to simultaneous annealing effect of lattice. That is why more dense and conducting ZnO:Al films were deposited. The surface of ZnO thin film is textured and rough, so that this surface is very much suitable for light scattering in a synchronized manner. On the other hand, TiO_2 film is highly transparent, compact and has higher value of refractive index 2.44 with anatase crystalline phase deposited at $T_s = 450^0$C. Fine roughness value of TiO_2 thin films is effective for minimization of light scattering. Here proper matching with individual film thickness and refractive index of the above two materials creates constructive interference in infrared region, and hence the combined bilayer coating gives more that 60% infrared reflection.

4. Conclusions

TiO_2/ZnO bilayer film with high infrared reflection property has been developed by RF-magnetron sputtering for heat reflector coating application. The bilayer coating has 80%visible transmission and 60% IR transmission with plasma resonance frequency near 1200nm. The refractive index of ZnO and TiO_2 films are 1.5 and 2.44 respectively. The surface roughness of TiO_2 and ZnO films are 1.95nm and 13.2nm respectively. The combination of high-low refractive indices materials with individual layer thickness 48nm and 420nm, and the above mentioned materials properties are very much effective to achieve the desired optical reflection in infrared region.

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References

[1] K. L. Chopra, S. Major and D. K. Pandya: *Thin Solid Films* 102 (1983) 1.

[2] Y. Sawada and Y. Taga: *Thin Solid Films* 110 (1983) L129.

[3] Z.-C. Jin, I. Hamberg and C. G. Granqvist: *Appl. Phys. Lett.* 51 (1987) 149.

[4] **R. Das** and S. Ray: *J. Phys. D* 36 (2003) 152.

[5] Y. Sawada and Y. Taga: *Thin Solid Films* 116 (1984) L55.

[6] B.O'Regan, M.Grätzel, *Nature* 353 (1991) 737.

[7] K. Tennakone, C.T.K. Tilakaratne, I.R.M. Kottegoda, *J.Photochem.Photobiol.* A 87 (1995) 177.

[8] K. Vinodgopal, S. Hotchandani, P.V. Kamat, *J. Phys. Chem.* 97 (1993) 9040.

[9] H. Tada, H. Honda, *J. Electrochem. Soc.* 142 (1995) 3438.

[10] W.Kern, E. Tracy, *RCA Rev.* 41 (1980) 132.

[11] Bose S, Ray S and Barua A K, *J. Phys. D: Appl. Phys.* **29** (1996) 1873

[12] Y.Igasaki and H.Kanma: Appl. Surf. Sci., 169- 170, (2001) 508.

[13] T. Minami, K. Oohashi, S. TakataT. Mouri and N. Ogawa, *Thin Solid Films* 193-194, (2) (1990), 721.

[14] Kluth O, Rech B, Houben L, Wieder S, Sch¨ope G, Beneking C, Wagner H, L¨offl A, Schock H W *Thin Solid Films* **351** (1999) 247.

[15] Hiroshi Kumagai, Yuji Tanaka, Yusuke Masuda, Tsutomu Shinagawa and Ataru Kobayashi; *Transactions of the Materials Research Society of Japan,* 34[4], (2009) 605.

[16] Sonya Calnan, *Coatings*, 4, (2014) 162-202;

[17] **Rajesh Das** and Swati Ray; *Japanese Journal of Applied Physics, 44, (2005) 1367.*

[18] K. Nagai, H. Kumagai and Y. Masuda; *IOP Conf. Series: Materials Science and Engineering* 24 (2011) 012021.

[19] A.Goodman, Applied Optics, 17 (2779) 1978.

Table-1: Variations of Deposition rate (R_d), Sheet resistance (R_{sh}) and Resistivity (ρ) of ZnO films with different Oxygen concentration ratio at 300^{0}C

Gas ambient	$[O_2/(Ar+O_2)] \times 100\%$ (C_O)	Deposition rate (R_d) (Å/min)	Sheet resistance (R_{sh}) (Ω/□)	Resistivity (ρ)(Ω-cm)
$Ar+O_2$	0	69	15	8.6×10^{-4}
	4	55.5	25	3.2×10^{-3}
	10	53	600	5.6×10^{-2}
	20	48	1700	1.3×10^{-1}

Table-2: Estimation of Refractive Index, Film Thickness from Transmission and Reflection spectra of TiO_2 films measured by UV-VIS-NIR spectrophotometer

Sl. No.	RF Power (Watt)	Wavelength corresponding to maximum peak (λ_{max})(nm)	Wavelength corresponding to minimum peak (λ_{min})(nm)	Transmittance Minima(T_m)	Refractive index of TiO_2 thin films (n_1)	Film thickness (d) (nm)
1.	60	859.27	535.58	77.96	2.44	291.5
2.	80	558.98	805.97	72.81	2.37	385.4
3.	100	698.07	1006.16	74.01	2.38	478.25

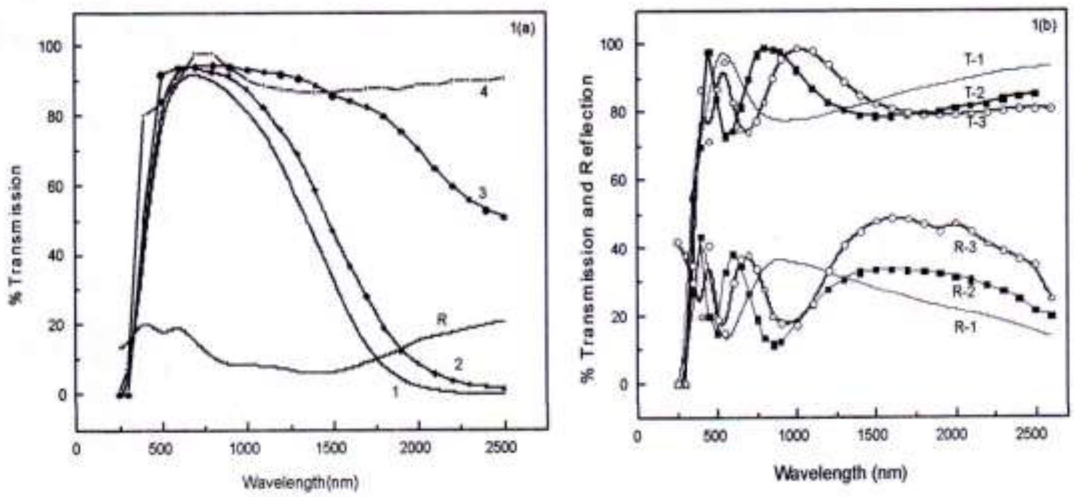


Figure 1: Optical Transmission (%T) and Reflection (%R) of (a) ZnO:Al thin films with 1-C_O= 2%, C_O= 4%, C_O= 10%; and C_O= 20%, and (b) TiO_2 thin films deposited at 1-60 watt; 2-80 watt and 3-100 watt respectively.

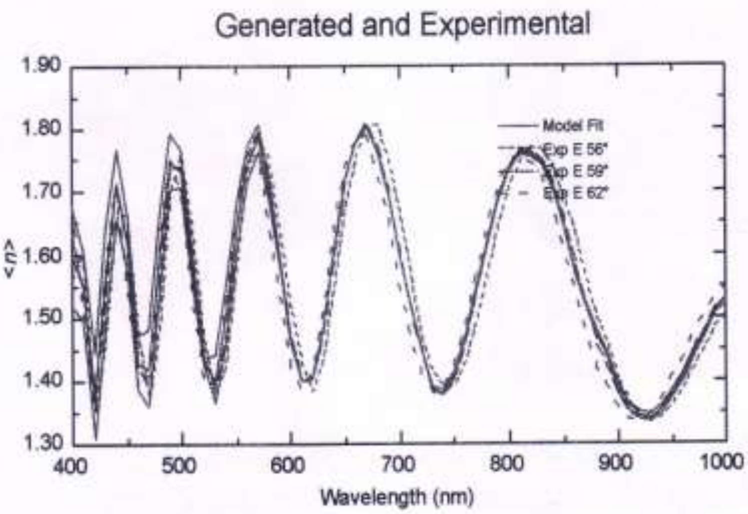
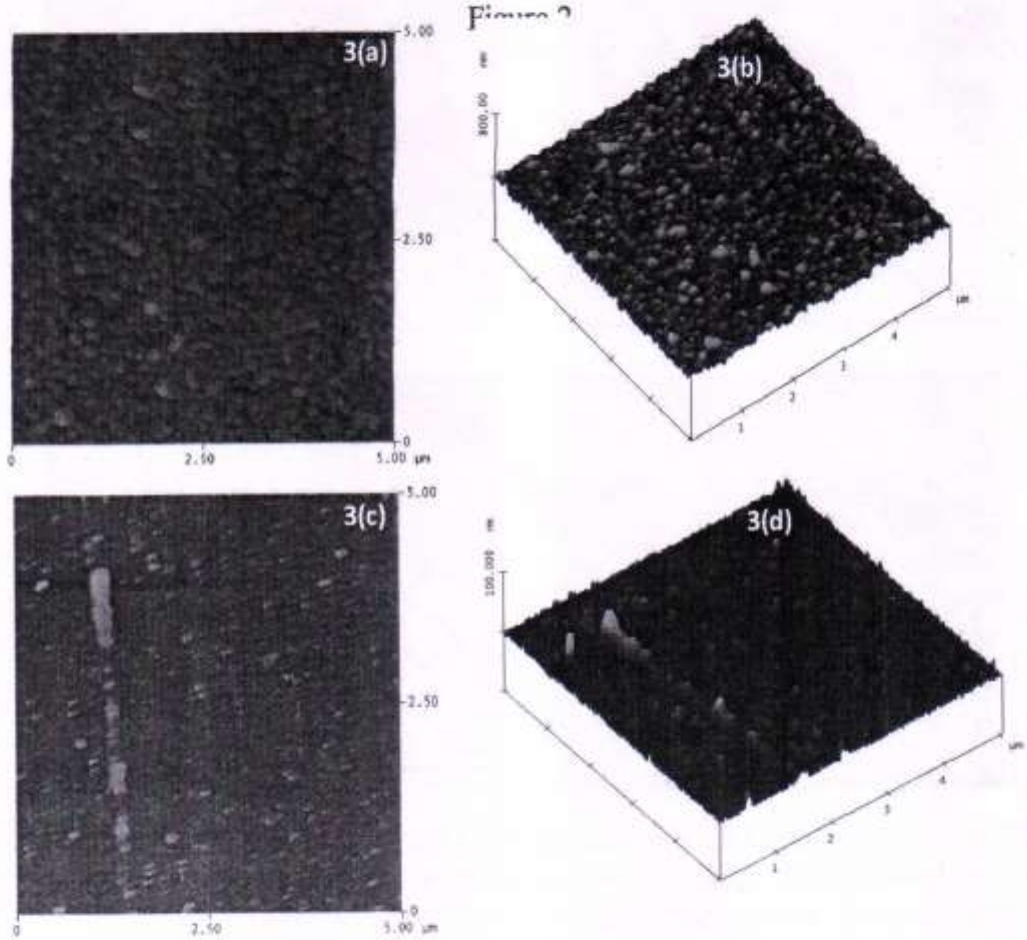


Figure 2: Ellipsometric data for the real part of refractive index ZnO:Al thin film (C_O= 2%)

Figure 3



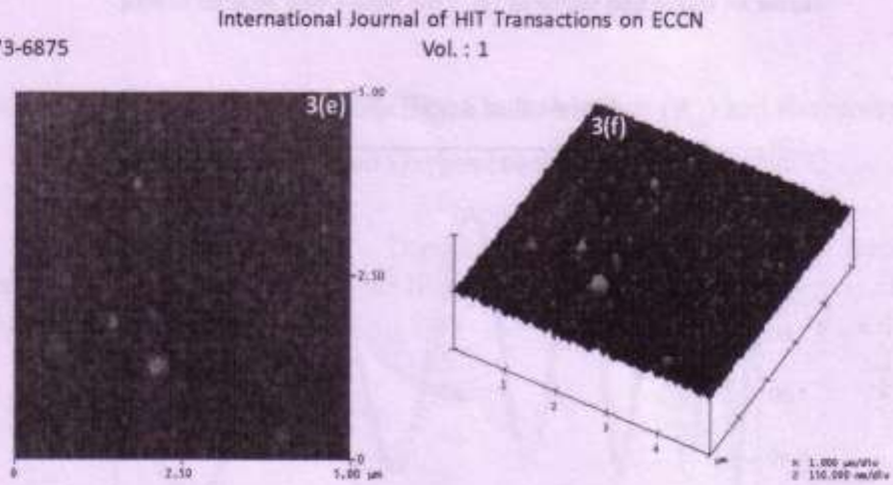


Figure 3: AFM image (2D and 3D topography) of (a,b) ZnO:Al films under Ar+O_2 (C_O = 2%), (c,d) TiO_2 film (e,f) TiO_2/ZnO:Al bilayer films respectively.

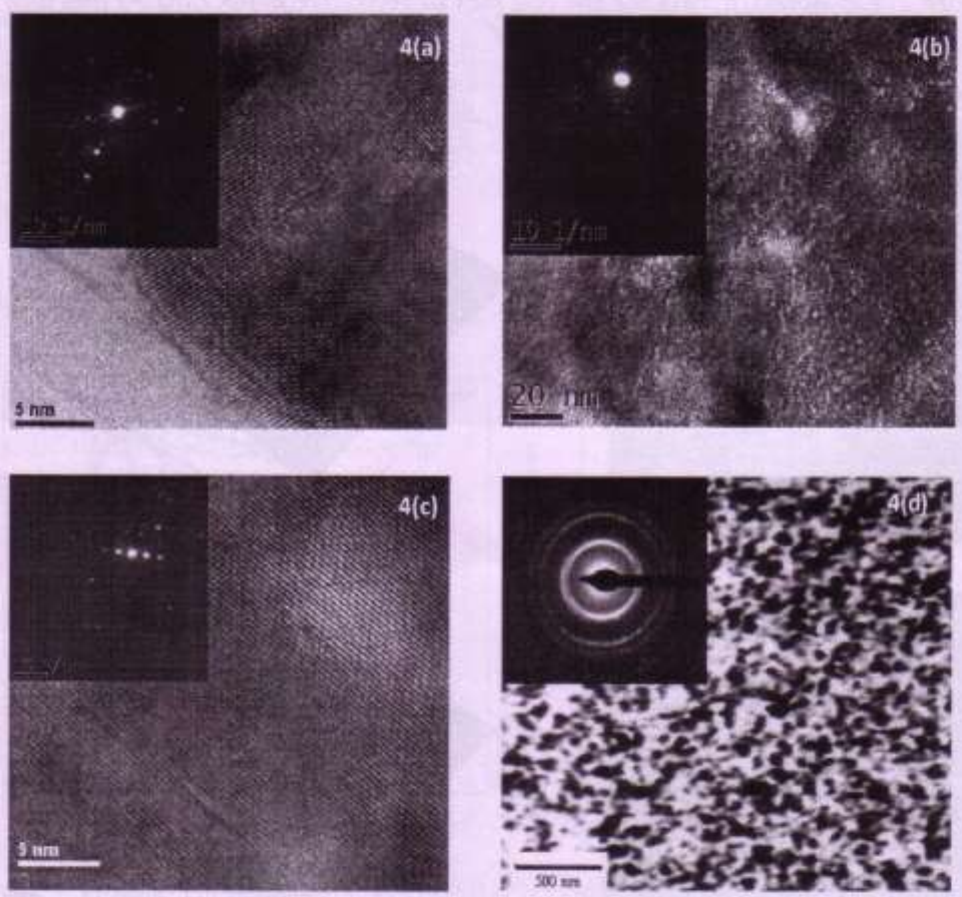


Figure 4: Transmission Electron Micrograph (TEM) and Diffraction (TED) pattern of TiO_2 film deposited under substrate temperature 450°C at (a) 100 watt, (b) 80 watt, and (c) 60 watt respectively; and (d) ZnO:Al film

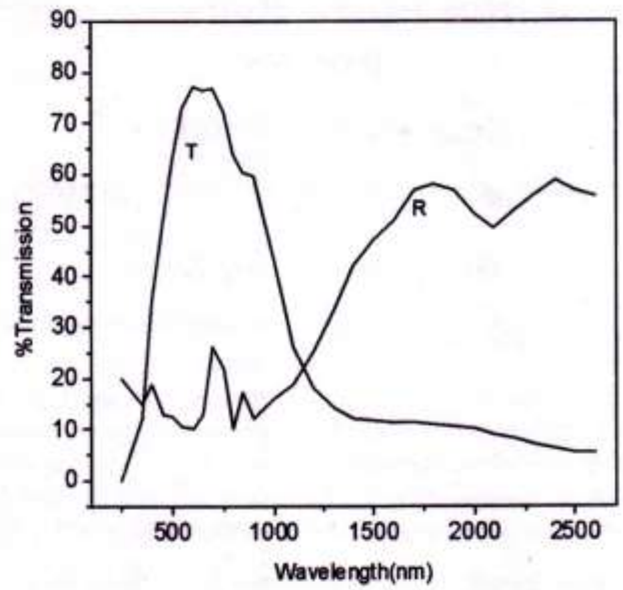


Figure 5: Optical Transmission (%T) and Reflection (%R) of TiO_2/ZnO:Al bilayer film