INVESTIGATIONS ON TiO_2 AND Ag BASED SINGLE AND MULTILAYER FILMS FOR WINDOW GLAZINGS

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ABSTRACT

In this investigation, TiO_2 and Ag based single and multilayer-films were deposited on microscope glass slides with varying individual layer thicknesses by radio-frequency reactive magnetron sputtering. Prior to multilayer development, single layers of Ag and TiO_2 were deposited and characterized. All the films were prepared at an elevated pressure of 3 Pa at room temperature. It was found that single layer of TiO_2 showed anatase polycrystalline structure. It also exhibited high visible transmittance of above 80% and higher refractive index of 2.31 at a wavelength of 550 nm. The indirect optical band gap of the TiO_2 films was estimated as 3.39 eV. The Ag single layer films were found to be crystalline with a very high reflectance for IR (Infra-red) light. Finally, the multi-layers have been deposited and characterized by X-ray diffraction, UV-visible-NIR spectro-photometry, scanning electron microscopy and Auger electron spectroscopy.

Keywords: multilayer coatings, dielectric material, structural properties, optical properties, window glazing.

INTRODUCTION

As one of the important dielectric layer with wide-band-gap (Eg>3 eV) and high refractive index, titanium dioxide (TiO_2) has been subject to extensive academic and technological research for decades. For its remarkable optical properties, today thin films of TiO_2 are frequently employed for many optical devices in optics industry [1] and solar cells [2]. The highly transparent TiO_2 films can be used as anti-reflection coatings for increasing the visible transmittance in the photo catalytic heat mirrors [3]. High transmittance in the visible region (λ = 380-760nm) is one of important optical requirements for the heat mirror. It can be achieved by the optimization of the deposition techniques. TiO_2 can exist as an amorphous layer and also in three crystalline phases: anatase (tetragonal), rutile (tetragonal) and brookite (orthorhombic). Only rutile phase is thermodynamically stable at high temperature. Antase TiO_2 mainly contributes to the photo-catalysis for the multilayer. The refractive index at 500 nm for anatase and rutile bulk titania is about 2.5 and 2.7 respectively [4]. There are many deposition methods used to prepare TiO_2 thin films, such as electron-beam evaporation [5], ion-beam assisted deposition [6], DC reactive magnetron sputtering [7], RF reactive magnetron sputtering [8], sol-gel dip coating method [9], sol-gel spin coating method [10], chemical vapor deposition[11] and plasma enhanced chemical vapor deposition [12].

The properties of the titanium dioxide films depend not only on the preparation techniques but also on the deposition conditions. PVD (Physical vapor deposition) technology is still a mainstream production tool for functional coatings. Sputter deposition techniques are widely utilized methods in industrial products because the high quality films with better mechanical property can be obtained at low substrate temperature with good uniformity of the film thickness in a large area. For window glazing, oxide films should possess a high transmittance and a high refractive index in the visible range of light spectrum with negligible absorption index or extinction coefficient [13]. From the literature, it is observed that titanium oxide films used in multilayer systems for window glazings are usually deposited on soda-lime glass substrates by electron beam evaporation [4, 13, 14, 15]. So far from the literature, it is found that Fan and Bachner [16] reported radio-frequency (RF) argon sputtered titanium oxide films from ceramic target (TiO_2) for preparing TiO_2/Ag/ TiO_2 multilayer films utilized in window glazings.

However, in the present study, TiO_2 and Ag films with various thicknesses have been deposited by RF magnetron sputtering at an elevated deposition pressure. Later the multilayer stacks of TiO_2/Ag/TiO_2 have been deposited with varying Ag film thickness. Finally, it has been attempted to discuss those films in the perspective of structural, optical and morphological properties.

EXPERIMENTALS

In this work, TiO_2, Ag and the multi-layers were prepared on microscope glass slides by radio-frequency (RF) magnetron sputtering using Ti (99.99%) and Ag (99.99%) targets. TiO_2 films were grown by reactive sputtering under a mixture of 46 sccm of Ar (99.999%) and 10 sccm of O_2 (99.999%). The sputtering chamber was evacuated down to 5×10^{-4} Pa and the working pressure was kept at 3 Pa. During the depositions, the RF power was 250 W. Ag films were prepared using 65 sccm flow of Ar and 50 W RF power with an Ag target of 4 N purity. For the multi-layers, the same conditions were maintained. The crystalline quality of the deposited films were investigated by X-ray diffraction (XRD) measurements (Model-D5000, Siemens) in θ-2θ geometry using Cu K_α radiations (λ = 0.15406 nm). The NanoTest system by Micro Materials Ltd., UK was used for micro-scratch tests. The UV-visible-NIR optical transmission spectra of TiO_2 thin films were recorded by a double-beam spectrophotometer (Jasco 570). The surface morphological features were observed by a field emission scanning electron microscope (FESEM). The thicknesses of the individual TiO_2 and Ag films were measured by SEM and a surface profiler (Tencor Alpha Step 200), respectively. The depth profiles of the sample deposited at 300 ºC were analyzed by Auger electron spectroscopy (Jeol-JAMP 9500F field emission scanning Auger microprobe, Japan).

RESULTS AND DISCUSSIONS

Characterization of TiO_2 and Ag films

It has been shown in our earlier report [17] that the thickness of the TiO_2 film measured by SEM was approximately 340 nm. The TiO_2 film deposited at room temperature and at an elevated pressure of 3 Pa was found to be polycrystalline having anatase phase only as shown in Figure-1. The reason may be that the kinetic energy of the impinging particle is high enough to initiate crystallization. Sung and Kim *et al.*, [2] also observed anatase phase in their titania films deposited by sputtering at an elevated pressure. The stronger diffraction was found along the anatase (101) crystal plane. From full width at half maximum (FWHM) of the diffraction peaks one may estimate the average grain size of polycrystalline materials by applying Scherrer formula [18].

Based on the dominant diffraction peak (101), it is estimated that the grain size is about 44 nm. Figure-1 shows the XRD spectrum of the 330 nm thick Ag film where the thickness was measured by a surface profiler.

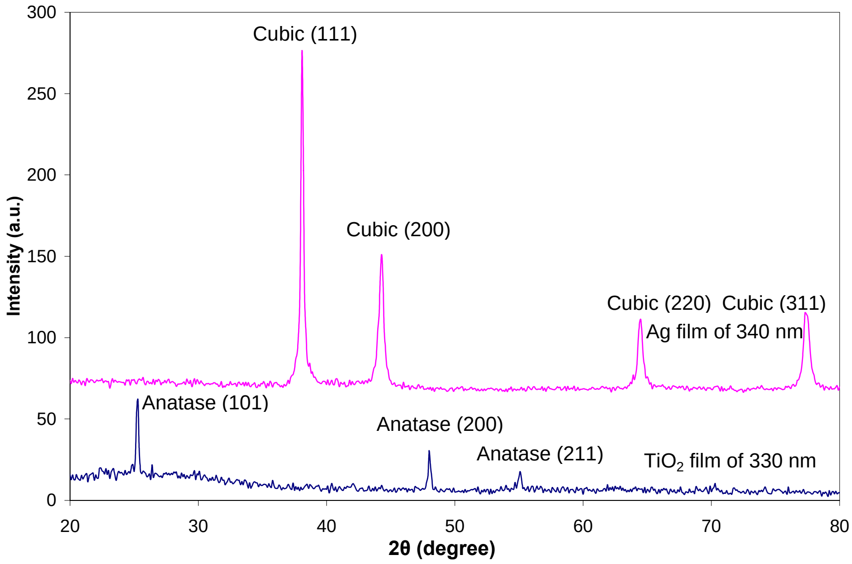

Figure-1. XRD spectrum of TiO_2 and Ag films deposited on microscope slide.

It is observed that as-deposited Ag film at room temperature is found to be crystalline and possesses stable cubic structure as it shows few strong peaks along planes of (111), (200), (220) and (311). The appearance of many peaks indicates the polycrystalline nature of the film. The preferential orientation of the crystals is found to be along the (111) crystal plane. The origin of the preference is the fact that (111) is the lowest energy plane in the fcc (face centered cubic) structure. For a high Ar pressure almost similar to ours, same poly-crystallinity has been previously observed for Ag films prepared by rf magnetron sputtering at room temperature [19]. The grain size determined via the Scherrer formula for Ag film is found to be 34 nm which is in good agreement with the mentioned research findings [19].

Optical characterization revealed that the TiO_2 film exhibited high visible transmittance of above 80% and higher refractive index of 2.31 at a wavelength of 550 nm. The indirect optical band gap of the TiO_2 films was estimated as 3.39 eV. Micro-scratch tests reveal that the adhesion critical loads and the scratch hardness of TiO_2 films deposited at room temperature are found to be 1.51 N and 11.5 GPa, respectively. Therefore, it can be thought that titanium oxide films deposited at room temperature exhibit better mechanical properties as well.

Optical properties of single and multilayer structures

Several thin films of silver having approximate thickness of 18, 20 and 22 nm were prepared at a sputtering pressure of 3 Pa. The transmittance curves of those films found using UV-VIS-NIR spectrophotometer is shown in Figure-2. It is seen that visible transmittance decreases with the increase of silver film thickness. The infra-red transmittance at 2500 nm for all these films is observed to be smaller than 5% and decreases slightly with the increase of film thickness. As the films are very thin, absorbance of light can be considered negligible. So, it can be inferred that all the films show very high infra-red reflectance. The highest infra-red reflectance occurs for the Ag film having 22 nm thickness. Using different thickness of Ag films, different multilayer stacks of TiO_2/Ag/TiO_2 films were prepared and shown in Figure-3. From the Figure, it is observed that transmittance in the visible light region of 380-750 nm decreases with the

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increase of Ag film thickness. But none of the films exhibits low transmittance in the infra-red portion of light. Therefore, the films do not possess high IR reflectance or heat mirror effect. The film with the thickest Ag film shows the highest IR reflectance. Considering Ag film of 20 nm thickness, TiO_2/Ag/TiO_2 and TiO_2/Ag were developed and shown in Figure-4. The Figure also shows the transmittance curves of thin titanium oxide (35 nm) and silver films (20 nm). It is observed that thin titanium oxide film shows high transmission of light in visible and infra-red region. Ag film shows very low transmittance in the infra-red region. TiO_2/Ag film is seen to have visible

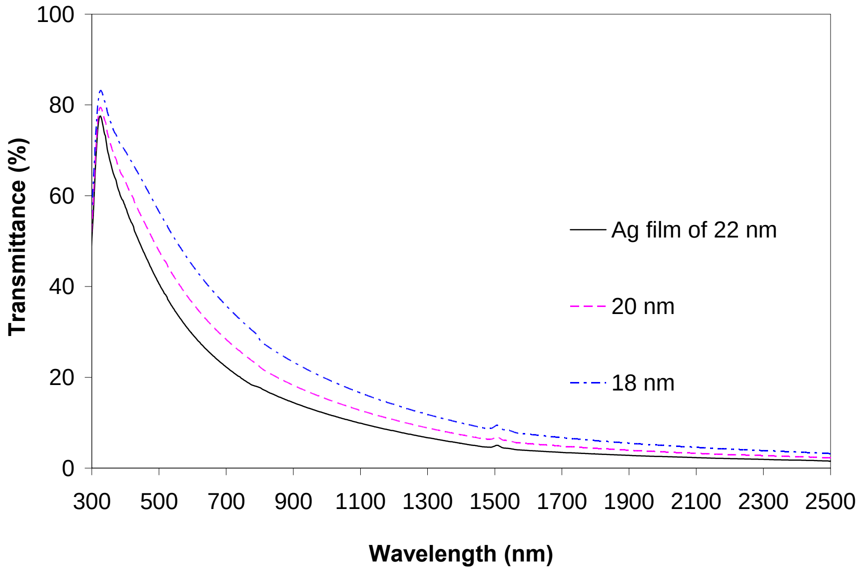

Figure-2. Variation of transmittance for the thin Ag films deposited at room temperature.

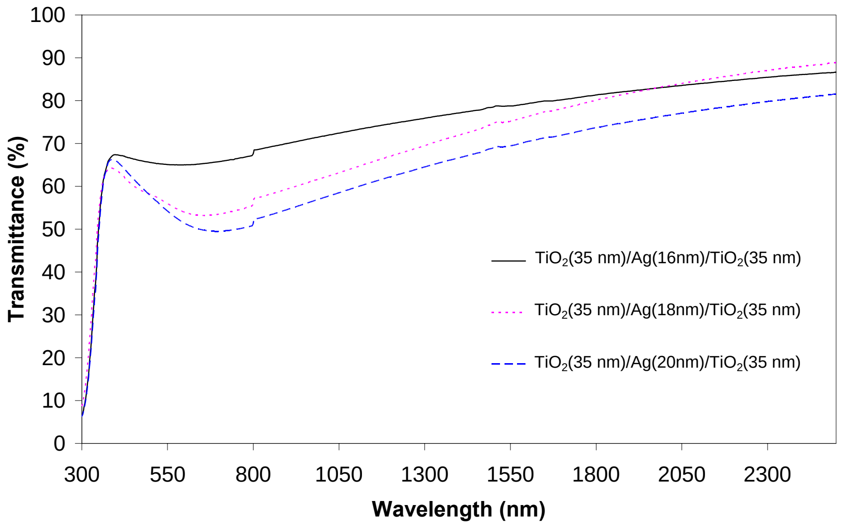

Figure-3. Transmittance spectra of TiO_2/Ag/TiO_2 films with different Ag film thickness.

transmittance of about 40% and low infra-red transmittance (about 25% at 2500 nm) compared to the triple layer structure. It indicates limited heat-mirror effect. But for the triple layer film of TiO_2/Ag/TiO_2, high infra-red transmittance is observed.

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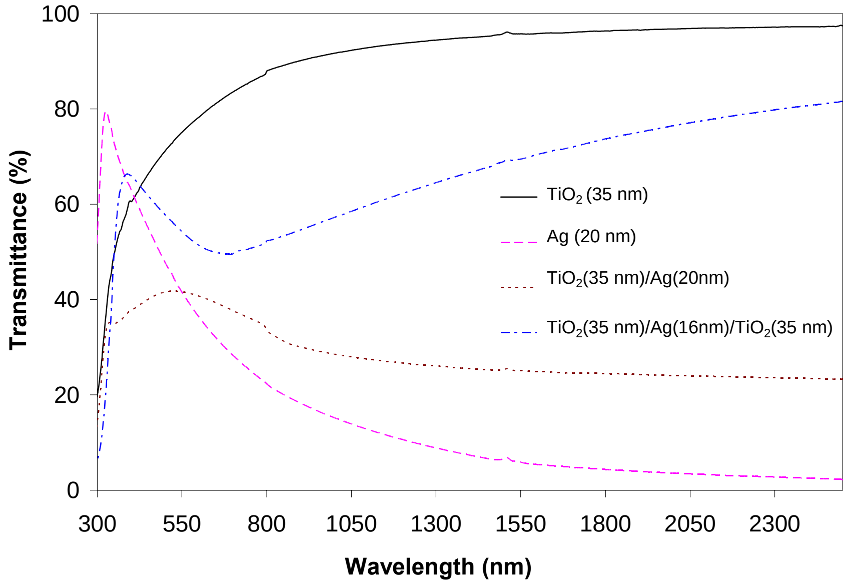

Figure-4. Transmittance curves of single and multilayer films of TiO_2 and Ag.

From the literature, several reports are found to investigate optical behavior of $TiO_2/Ag/TiO_2$ films deposited on glass substrates at a comparable thickness in this present work. Several works [4, 13, 15] developed inner and outer TiO_2 layers using ceramic targets of TiO_2 by electron beam evaporation. The middle Ag films were prepared by thermal evaporation. All those works reported high visible transmittance and very low transmittance at infrared range. Fan and Bachner [16] reported similar transmittance values for $TiO_2/Ag/TiO_2$ films prepared by RF argon sputtering of TiO_2 and silver targets. Tachibana *et al.*, [20] observed low visible transmittance for five layer stacks of TiO_2 and Ag. In that work, TiO_2 films were deposited by DC magnetron sputtering of ceramic target (TiO_{2-x}) at an argon and oxygen atmosphere where oxygen content is only 3% of total mixture. In this research, titanium oxide films were deposited by RF reactive magnetron sputtering of titanium target using higher content of oxygen. The flow rate of argon and oxygen used were 45 and 15 SCCM, respectively.

Morphological properties of single and multilayer structures

Figure-5a-g shows surface morphology of thin TiO_2 film (35 nm), TiO_2/Ag and $TiO_2/Ag/TiO_2$ films at low and high magnification under the FESEM. From the figure, it is clear that at low magnification (X1000), TiO_2 and TiO_2/Ag films are found to be flat with

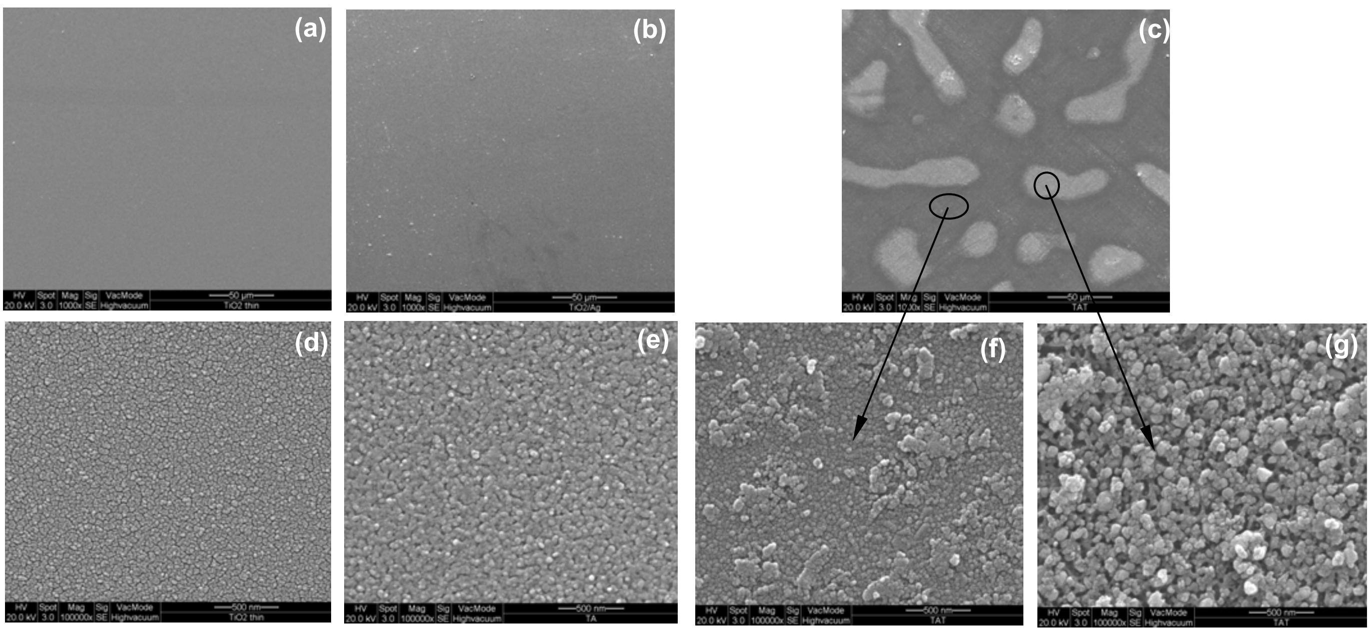

Figure-5. FESEM micrographs of (a) TiO_2, (b) TiO_2/Ag, (c) $TiO_2/Ag/TiO_2$ films at low magnification (1000X), (d) TiO_2, (e) TiO_2/Ag, (f) and (g) $TiO_2/Ag/TiO_2$ films at high magnification (100,000X).

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homogenous morphology. But the triple-layer film (Figure-5c) shows different surface areas (dark and bright). It indicates an inhomogeneous film formation for the $TiO_2/Ag/TiO_2$ film. The film growth of TiO_2 on glass substrate and Ag on TiO_2 coated glass substrate is found to be uniform and free from any defects. Besides, SEM images at high magnification for TiO_2 and TiO_2/Ag are found to be flat and homogenous. Dark and bright areas of $TiO_2/Ag/TiO_2$ film at high magnification shows completely different morphology. Dark area shows film growth defects having non-uniform and agglomeration of materials. Bright area shows agglomeration of particles with a large number of holes around the surface. SEM images at high magnification indicate higher surface roughness for the $TiO_2/Ag/TiO_2$ film.

Auger electron spectroscopy (AES) analysis

AES depth profile of TiO_2/Ag film, as shown in Figure-6, exhibits the quality of interface between silver and titanium oxide films. It is observed that two layers of Ag and TiO_2 are easily distinguishable. Some intermixing of different elements in the narrow region of the interface might have happened. But two layers of Ag and TiO_2 are easily distinguishable. This supports the lower transmittance obtained in the infra-red region of light which indicates better heat-mirror effect of TiO_2/Ag film (Figure-4). Silver is found to diffuse through TiO_2 film up to the glass substrate. The reason of not getting the maximum heat-mirror effect is due to intermixing of the elements in the interface and the diffusion of silver into TiO_2 film. Figure-7 shows the AES depth profiles for $TiO_2/Ag/TiO_2$ film were also investigated to see the

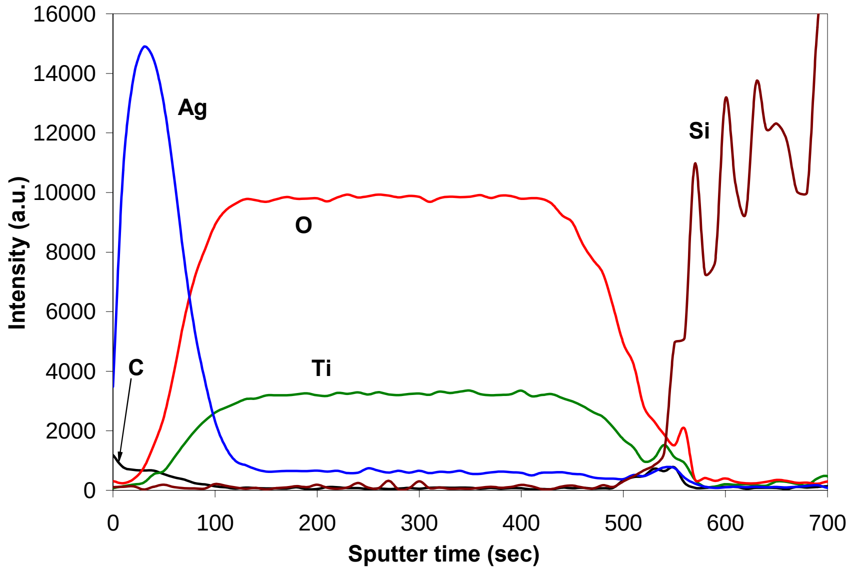

Figure-6. AES depth profile of TiO_2/Ag film deposited on glass substrate.

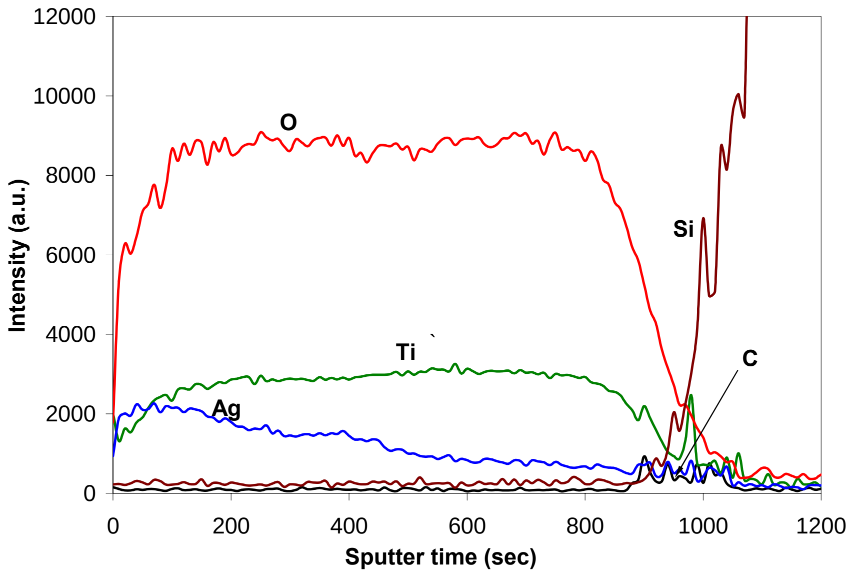

Figure-7. AES depth profile of $TiO_2/Ag/TiO_2$ film deposited on glass substrate.

elemental distribution of the multilayer. From Figure-7, it is observed that there is strong intermixing of different elements which practically results in a single layer structure having titanium and oxygen at a uniform proportion. Ag is observed to be diffused into both inner and outer TiO_2 films. It is thought to joining of inner and outer TiO_2 films and the diffusion of Ag film into these films.

CONCLUSIONS

Both as-grown titanium oxide and silver films prepared at room temperature were found to be polycrystalline. As-grown TiO_2 film exhibited high visible transmittance of above 80% and higher refractive index of 2.31 at a wavelength of 550 nm. Single layer Ag films of nanometric thickness (18-22 nm) exhibited very low infra-red transmittance (below 10%) with moderate visible transmittance. A bi-layer TiO_2/Ag film is seen to have visible transmittance of about 40% and low infra-red transmittance (about 25% at 2500 nm) which showed limited heat-mirror effect. But for the triple layer film of TiO_2/Ag/TiO_2, high infra-red transmittance is observed. SEM micrographs revealed that film growth of titanium oxide films on Ag films was poor. AES results clearly showed little intermixing of layers for bi-layer TiO_2/Ag film, but high intermixing were observed for the tri-layer structure of TiO_2/Ag/TiO_2 films. Higher content of oxygen for depositing outer TiO_2 layer are thought to be the reasons for intermixing of all three layers in tri-layer films.

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