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Short Communication

Hydrogen Plasma Annealed Titanium Dioxide Oxide/Aluminum-doped Zinc Oxide Films Applied in Low Emissivity Glass

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This study applies titanium dioxide oxide/aluminum-doped zinc oxide (TiO_2/AZO) films on glass as low-emissivity glass to allow self-cleaning. The AZO and TiO_2 layers respectively allow low-emissivity and self-cleaning. Previous studies of TiO_2 films introduce Ti^{3+} and oxygen vacancies during the hydrogen plasma treatments process to increase the hydrophilic nature of the surface. This study anneals TiO_2/AZO using hydrogen plasma to increase the hydrophilic nature of TiO_2/AZO. TiO_2/AZO films are deposited on glass substrates and then undergo hydrogen plasma treatment. AZO films also undergo hydrogen plasma treatment and the electrical resistivity is measured. The experimental results show that hydrogen plasma treatment of TiO_2/AZO samples affects the structure, contact angle, and emissivity. The average roughness value for TiO_2/AZO films decreases after hydrogen plasma treatment. The water contact angle for TiO_2/AZO films decrease from 67.28° to 10.10° after hydrogen plasma annealing. After 1 hour of ultraviolet (UV) irradiation, the contact angle further decreases to 7.04°, so the films develop a super-hydrophilic surface. The emissivity, the water contact angle and the average visible transmittance for TiO_2/AZO films that undergo hydrogen plasma treatment is 0.20, 7.04° and 83.01%, respectively. These results indicate a super-hydrophilic surface that is within the range for low emissivity glass.

Keywords: TiO_2/AZO; hydrogen plasma treatment; low emissivity glass

1. INTRODUCTION

Low-emissivity (low-e) features high transmittance in the visible spectrum and high reflectivity at infrared wavelengths. Low-e glass is widely used in buildings [1, 2]. Emissivity is used to determine the heat-insulating capability of low-e glass. Thin films of silver metal are often used to produce low-e glass. Silver films have good electrical conductivity and reflect heat effectively but they are easily oxidized and adhere poorly to glass substrates.

Previous studies use substitutes for silver films to produce low-e glass. Transparent conductive oxide (TCO) materials feature high visible light transmittance and low electrical resistivity. TCO is used for many types of energy-saving glass and solar cells [3-6]. The most commonly used TCO series is indium tin oxide (ITO) but ITO contains Indium, which is expensive and toxic. AZO is an alternative to ITO because AZO is a non-toxic, less expensive and abundant.

Previous studies show that post-treatment reduces the electrical resistivity of AZO films. Hydrogen plasma treatment and annealing in a hydrogen atmosphere are common methods [7-10]. Desorption of negatively charged oxygen species at the grain boundaries and/or Zn^{2+} ions are replaced by Al^{3+} ions [11-15]. The negatively charged oxygen species adsorbed at the grain boundaries of AZO play the role as electron trapping centers and form potential energy barriers so the free carrier concentration and hall mobility are decreased. Desorption of these negatively charged oxygen species during annealing increases the free carrier concentration and hall mobility. Hydrogen plasma treatment can make these negatively charged oxygen species desorbed away from the grain boundaries of AZO so the carrier concentration and carrier mobility increase [12, 13].

Previous study fabricated AZO/ITO films post-annealed using hydrogen plasma treatment [14, 15]. AZO/ITO that is annealed using hydrogen has a lower electrical resistivity and emissivity decreases as the film's electrical resistivity decreases. This result is in agreement with the Hagen–Rubens relationship, which states that the emissivity of a material is related to electrical resistivity [16].

Multi-functional low-e glass increases the functionality of low-e glass. Titanium dioxide is used to create self-cleaning glass [17-20]. The hydrophilicity of the TiO_2 surface increases when it is exposed to ultraviolet radiation because there is photo-induced hydrophilicity. If TiO_2 is irradiated with UV light, TiO_2 forms electron-hole pairs. Electrons tend to reduce from the Ti^{4+} to Ti^{3+} state and the holes oxidize O^{2-} to produce oxygen vacancies. Oxygen vacancies are occupied by water and hydroxyl radicals (•OH) are produced, so the TiO_2 surface becomes hydrophilic [19, 20, 21].

If glass that is coated with a titanium dioxide film is exposed to rain, water drops spread evenly across the hydrophilic surface to form a water film and dirt is carried away from the surface by the water film so the glass is self-cleaning [18, 20]. The hydrophilic properties of a surface are determined by measuring the water contact angle. The smaller the contact angle, the more hydrophilic is the material [18, 20]. The hydrophilicity of TiO_2 is related to the number of oxygen vacancies and Ti^{3+}. Previous studies show that gas plasma treatment using hydrogen, nitrogen and oxygen increases the hydrophilicity of TiO_2 [22-24]. Hydrogen plasma treatment creates electron-hole separation in TiO_2 and then enhances the surface-active states of TiO_2 by changing its electronic structure from $TiO_2(Ti^{4+})$ to $Ti_2O_3(Ti^{3+})$. This behavior makes positive contribution to the hydrophilicity of TiO_2 [25, 26].

Thermal oxidation with titanium is used to produce TiO_2 [27, 28]. Previous work fabricated TiO_2 /AZO films using thermal oxidation of titanium/AZO film at different temperatures [28]. The optimum temperature is 500°C. The TiO_2 /AZO films on glass are very hydrophilic and feature low-emissivity and high visible light transmittance.

This study reports the production of plasma-annealed TiO_2 /AZO films on glass trying to give low-e with self-cleaning properties. The titanium oxide/aluminum-doped zinc oxide (TiO_2/AZO) is deposited on glass to produce low-e glass using the optimum temperature for thermal oxidation of 500°C [28]. The TiO_2/AZO films are post-annealed in hydrogen plasma to improve the hydrophilicity of the

TiO_2/AZO. The structural, electrical, optical and hydrophilic properties of as-deposited and hydrogen-plasma-treated TiO_2/AZO films are compared.

2. EXPERIMENTAL METHOD

TiO_2/AZO films were fabricated on a borosilicate glass. The glass was ultrasonically cleaned in acetone, isopropanol and purified water and dried using a dry nitrogen purge. AZO films were deposited on glass substrates using an in-line sputtering system. An AZO layer with a thickness of about 500 nm was sputtered using an AZO target ($ZnO:Al_2O_3$ = 98.5:1.5 wt.% size 760×136mm^2) at a DC power of 2kW, an Ar gas flow of 440 sccm and a working pressure of 3×10^{-3} torr.

Titanium films were deposited on AZO films by electron beam evaporation to fabricate Ti/AZO films. The deposited titanium film had a thickness of 100 nm. The evaporation chamber was evacuated to 3×10^{-6} torr. During evaporation of the films, the output power of the electron gun was maintained at 8 kW. The turntable was rotated at 6rpm during the deposition process. Ti/AZO was oxidized to form TiO_2/AZO by thermal oxidation [28] in a thermal annealing system in oxygen at 500 °C for 10 min using an oxygen gas flow rate of 100 sccm.

TiO_2/AZO and AZO films on glass were then post-annealed using microwave hydrogen plasma for 1 minute plasma at 600W, using a gas pressure of 35 torr and a hydrogen flow rate of 100 sccm. TiO_2/AZO films samples without and with hydrogen plasma annealing were respectively named as samples S_1 and S_2.

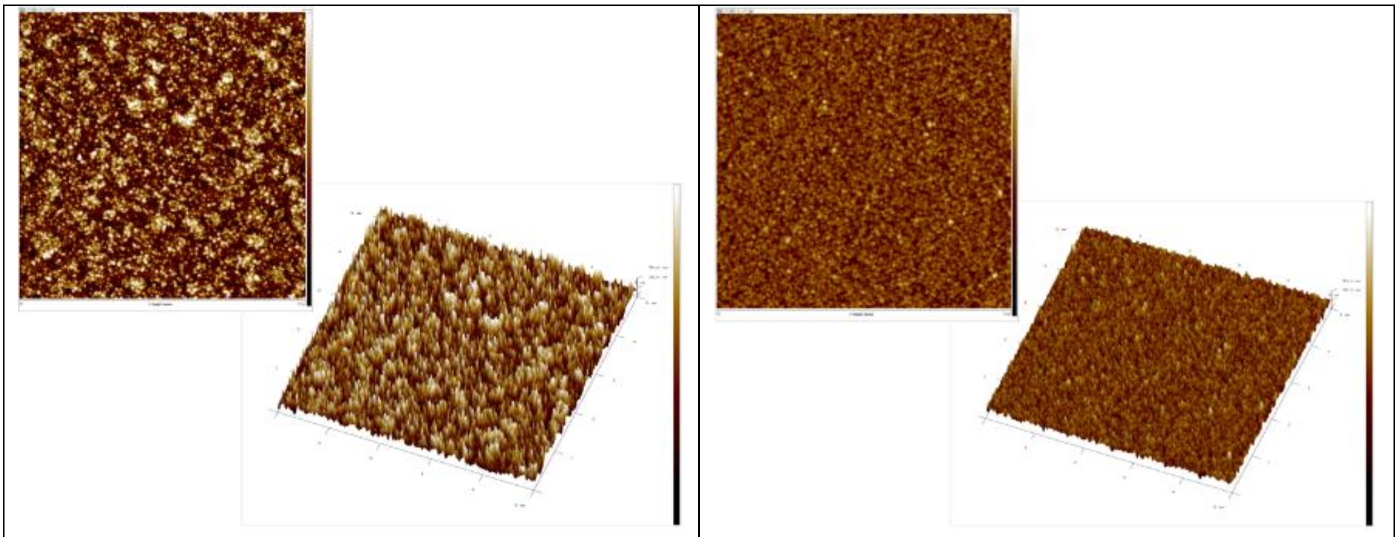
The surface roughness of S_1 and S_2 films was measured using a scanning probe microscope (SPM, Bruker ICON3-SYS, Bruker, Siegsdorf, Germany). The surface morphology of the S_1 and S_2 films was observed using a scanning electron microscope (SEM, SU8000, HITACHI, Tokyo, Japan). the crystalline structure of the S_1 and S_2 films was determined using an X-ray diffractometer (XRD, Rigaku D/Max2500, Rigaku, Tokyo, Japan). The optical transmittance of the S_1 and S_2 films was measured using a UV/VIS/NIR spectrophotometer (PerkinElmer LAMBDA 750, PerkinElmer, Waltham, U.S.A.) between wavelengths of 400 and 800 nm.

The hydrophilicity of the S_1 and S_2 films was measured using a contact angle meter (First Ten Angstroms FTA 1000B, First Ten Angstroms, Portsmouth, U.S.A.). The emissivity of the S_1 and S_2 films was measured using an emissivity meter (TSS-5X, Japan Sensor, Tokyo, Japan). The electrical properties of the AZO films was measured prior to depositing a titanium film. The carrier concentration, mobility, and electrical resistivity of the AZO films were measured using a Hall measurement (Hall effect measurement, Ecopia HMS-3000, Ecopia, gyeonggi-do, South Korea).

3. RESULTS AND DISCUSSION

The morphology and the average roughness (Ra) of the TiO_2/AZO samples without and with hydrogen plasma annealing (S_1 and S_2), as measured by SPM, are shown in Figure 1 and Table 1, respectively. The average respective roughness (Ra) values for S_1 and S_2 are 7.42 and 3.36 nm. The Ra value for TiO_2/AZO films decreases after hydrogen plasma annealing. A comparison of Figure 1(a) and Figure 1(b) shows that the plasma annealed TiO_2/AZO sample has a smoother surface.

Figure 2 shows the surface morphology images for S_1 and S_2, as measured using SEM. A comparison of Figures 2 (a) and (b) shows that the grains of the TiO_2/AZO films have a relatively small and uniform size after hydrogen plasma treatment. The SEM images show that the surface of the plasma-annealed sample is smoother. This result is in agreement with the measurements for the SPM micrographs in Figure 1 and Table 1.



(a) (b)

Figure 1. SPM images of the TiO_2/AZO films (a) before and (b) after hydrogen plasma treatment

Table 1 Structural and optical properties, contact angle and emissivity TiO_2/AZO films that undergo hydrogen plasma treatment**.** Structural properties: ZnO plane (002) and (103) peaks in the X-ray diffraction spectra and average roughness; optical properties: average optical transmittance in the visible range from 400 to 800 nm; contact angle: to measure the contact angles of water drops before and after UV irradiation; emissivity: the emissivity of TiO_2/AZO films is determined using an emissivity measurement.

Sample	ZnO Plane		Average roughness Ra(nm)	Average optical transmittance (%)	Emissivity	Contact angle	
	(002) 2θ (°)	(103) 2θ (°)				Before UV Irradiation	After UV Irradiation
S_1	34.44	62.92	7.42	81.34	0.59	67.28°	34.77°
S_2	34.46	63.00	3.36	83.01	0.20	10.10°	7.04°

X-ray diffractometer spectra for S_1 and S_2 are shown in Figure 3. Two diffraction peaks corresponding to the (002) and (103) of ZnO are clearly observed. The two theta values corresponding to the (002) and (103) peaks in the XRD spectra are listed in Table 1. The (002) and (103) peaks in the

ZnO spectrum shift to a greater angle if the TiO_2/AZO films are subject to hydrogen plasma annealing, so the adjacent (002) and (103) inter-planar distance for ZnO decreases if the film undergoes plasma treatment. More Al atoms substitute for Zn in the ZnO crystal lattice if TiO_2/AZO films undergo plasma treatment because the ionic and covalent radii of Al are smaller than those of Zn [29]. The position of the peak for the ZnO crystal plane shifts towards a higher angle if the film undergoes hydrogen plasma treatment These TiO_2/AZO films, are similar to those in a previous study by the authors [14, 15].

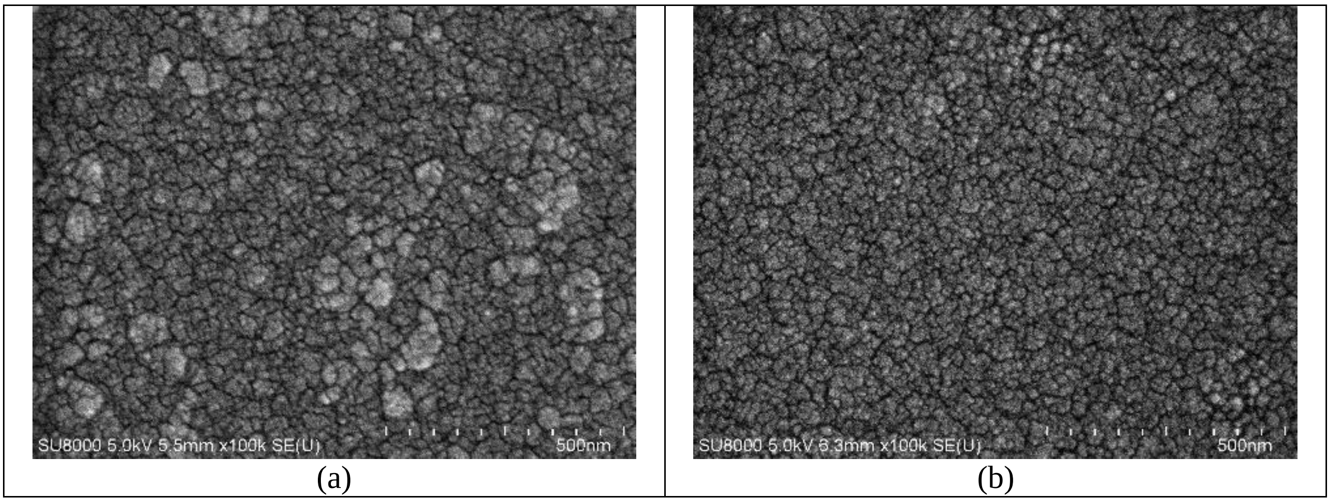


Figure 2. SEM micrographs of the TiO_2/AZO films (a) before and (b) after hydrogen plasma treatment

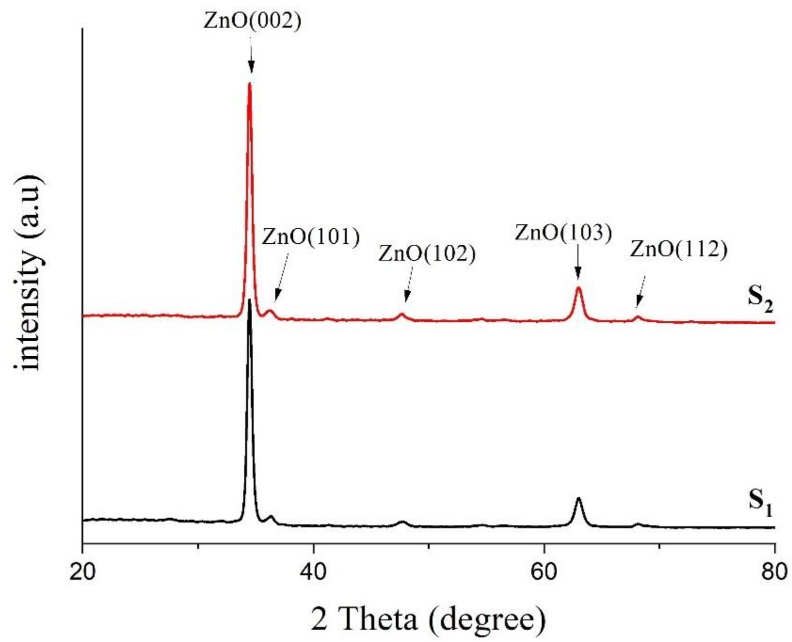


Figure 3. XRD spectra forTiO_2/AZO films before and after hydrogen plasma treatment

The optical transmittance spectra for S_1 and S_2, measured using a UV/VIS/NIR spectrophotometer, are shown in Figure 4. The average optical transmittance is 81.34% and 83.01% in the visible range from 400 to 800 nm for S_1 and S_2, as shown in Table 1. The average optical transmittance for TiO_2/AZO films that are annealed using hydrogen plasma is increased because the surface roughness of the films is small after hydrogen plasma treatment [30]. Flat films scatter less light when light arrives at the films' surface during optical measurement. The films have a smooth surface because they are bombarded by high energy ions in the plasma. This observation is in agreement with the SPM and SEM micrographs (Figure 1 (b) and Figure 2 (b)).

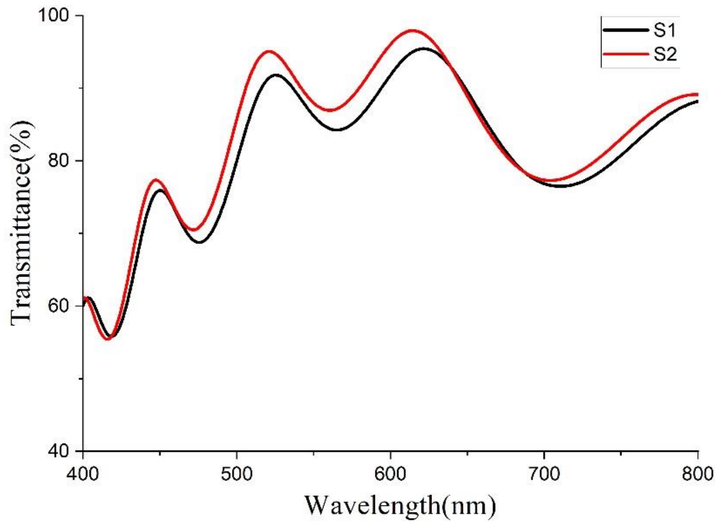


Figure 4. Optical transmittance spectra for TiO_2/AZO films before (black line; S_1) and after (red line; S_2) hydrogen plasma treatment

The hydrophilic properties of TiO_2/AZO films were determined by measuring the water contact angle for S_1 and S_2. Table 1 shows the water contact angle of samples, as measured using a contact angle meter before and after 1 hour of UV irradiations. The results show that the water contact angle decreases rom 67.28° to 10.10° if the sample undergoes plasma annealing. There is a decrease in the water contact angle because the TiO_2/AZO film is more hydrophilic. TiO_2/AZO films that undergo hydrogen plasma annealing are more hydrophilic because Ti^{3+} and oxygen vacancies are created when the plasma creates active surface states for the TiO_2/AZO film [23-26]. Hydrogen plasma annealing raises the surface-active states of TiO_2 by altering the electronic structure from $TiO_2(Ti^{4+})$ to $Ti_2O_3(Ti^{3+})$. Exposure to UV irradiation also results in a decrease in the water contact angle for S_1 (from 67.28 to 34.77°) and S_2 (from10.10 to 7.04°), as seen in the results in Table 1. This is explained by photocatalytic hydrophilicity [19-20].

Table 2. Electrical properties of AZO films that undergo hydrogen plasma treatment

Sample	Hydrogen plasma treatment	Carrier concentration ($10^{20}/cm^3$)	Carrier mobility (cm^2/Vs)	Electrical Resistivity ($10^{-3}\Omega$-cm)
AZO	Before	2.6	6.41	3.76
	After	5.7	13	0.86

The electrical resistivity, the carrier concentration and the mobility of AZO films with and without hydrogen plasma annealing are shown in Table 2. The electrical resistivity decreases and the carrier concentration and the mobility increase for AZO films that are annealed in hydrogen plasma. The improvement in the electrical properties of AZO films that undergo hydrogen plasma is in agreement with the results of previous studies [12-15]. Hydrogen plasma annealing raises carrier concentration resulted from (i) negatively charged oxygen species desorbed from the grain boundaries, which act as electron trapping centers, and (ii) creation of oxygen vacancies in zinc oxide to form free electrons. Plasma annealing also increases the Hall mobility because negatively charged oxygen species are desorbed from the grain boundaries act as electron potential barriers.

The respective emissivity of S_1 and S_2 samples is 0.59 and 0.20, as listed in Table 1. The emissivity of TiO_2/AZO that is annealed in hydrogen plasma is 77% less than the value for films that do not undergo plasma annealing. The lower the electrical resistivity of a film, the lower is its emissivity, as defined by the Hagen–Rubens relationship [16]. The results for emissivity in Table 1 and for electrical resistivity in Table 2 are in agreement with the Hagen–Rubens relationship.

The results for average visible transmittance, emissivity and water contact angle the key indices for low emissivity and self-cleaning glass in Table 1 show that TiO_2/AZO films on glass that are annealed in hydrogen plasma can be used to produce low emissivity and self-cleaning glass: 83.01% in average visible transmittance, 0.2 in emissivity and good hydrophilicity.

4. CONCLUSION

This study produces hydrogen-plasma-annealed TiO_2/AZO films on glass to to allow low-e and self-cleaning. The results show that hydrogen plasma annealing decreases the electrical resistivity and emissivity of TiO_2/AZO films with good hydrophilicity. The electrical resistivity of samples that undergo hydrogen plasma treatment is 77% less than for samples that do not undergo plasma annealing. The emissivity and the average transmittance (400~800 nm) TiO_2/AZO samples that are annealed in hydrogen plasma are 0.2 and 83.01%, respectively. The water contact angle for TiO_2/AZO samples after 1 hour of UV irradiation is 7.04°, which shows that the samples are super-hydrophilic.

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