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Thermal Stability of SnOx/NiCrOx/Ag/AZO/ SnOx/glass Multilayer Films Applied in Low-emissivity Glass

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Keywords： thermal stability, low-emissivity glass, silver

ABSTRACT

Low-emissivity glass is heat-block glass with high transmission in visible and high reflectivity in infrared region. Silver-based multilayer films is the potential candidate applied in low-emissivity glass compared with others. Low-emissivity glass usually needs high temperature process like bending or toughening process in industry. Characteristics of low-emissivity may deteriorate for low-emissivity glass after high-temperature process. The tin oxide/nickel chromium oxide/silver/ aluminum doped zinc oxide/tin oxide/glass (SnOx/NiCrOx/Ag/AZO/ SnOx/glass) and silver/aluminum doped zinc oxide/ tin oxide/glass (Ag/AZO/SnOx/glass) samples were produced by in-line sputtering. Part of the two samples was post treated with one hour and 500°C heat process. Microstructure, optical properties and emissivity of heated SnOx/NiCrOx/Ag/AZO/SnOx/ glass show no evident change compared with those of as-deposited samples. However, microstructure and optical properties apparently alter and the emissivity degenerate from 0.10 to 0.32 for heated Ag/AZO/ SnOx/glass samples. The outer layer: SnOx/ NiCrOx on Ag films can effectively prevent Ag agglomeration resulted from heat treatment. This paper contributes to the development of low-emissivity glass applied in energy-saving buildings.

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INTRODUCTION

Low-emissivity glass, which has high transmittance in visible wavelength and heat reflection, has been widely applied in energy saving architecture since 1977 (Martõn-Palma, R. J.et al., 1998). There are usually three kinds of materials applied for low-emissivity glass: 1. ultrathin metal films, 2. metal based multilayer films and 3. wide band gap with high concentration doped semiconductor films (Karlsson, B.et al., 1981). Selecting the optimum film thickness is difficult for the ultrathin metal films. The film thickness has to be thin enough to make the glass transparent in visible wavelength.

Meanwhile, the film thickness has to be thick enough to keep films flat for avoiding light absorption (Kusano, E.et al., 1986). Silver is the most commonly used metal in market due to its good electrical conductivity to provide heat reflection applied in low-emissivity. However, silver films are soft and have poor adhesion to the glass substrate. Protecting and interfacial films are often added on two sides of silver films. The sandwich structure in which silver is inserted between two dielectric films sketched in Figure 1.

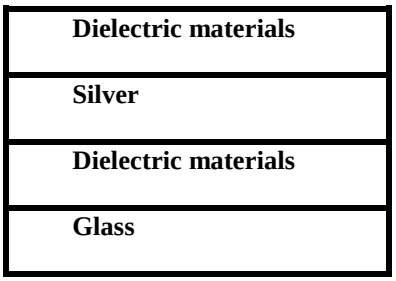


Figure 1. Basic silver-based sandwich structure of low-emissivity glass.

In addition to protecting metal films and aiding films adhesion with glass, the dielectric films play the role on interference layer for making low reflection in visible light and high reflection in the infrared region

(Huang, J.et al., 2014). Silver based low-emissivity films have been reported like In_2O_3/Ag/In_2O_3 (Qiu, D.et al., 2010), SnO_2/Ag/SnO_2 (Yu, S. H.,et al., 2012), ITO/Ag/ITO (Kim, T. H.,et al., 2010), ZnO/Ag/ZnO (Hajj, A. E.,et al., 2012), AZO/Ag/AZO (Ando, E.et al., 2001), TiAlN/Ag/TiAlN (Huang, J.et al., 2014), TiO_2/Ag/TiO_2 (Zhan, Q.et al., 2001). Recently, developing novel low-emissivity films adding multi-functional properties such as high transparency, anti-reflection, hydrophilicity and antifogging have been worth noted (Loka, C. et al., 2016). Toughening or vacuum forming in fabricating low-emissivity glass needs heat treatment (Meszaros, R.et al., 2012). Low-emissivity related properties might alter for silver-based multilayer films after heat treatment due to interlayer diffusion, grain growth, etc. Thermal stability of the multilayer films is a critical factor in processing low-emissivity films. This paper investigates the thermal stability of tin oxide/nickel chromium oxide/silver/aluminum zinc oxide/tin oxide/glass (abbreviated as SnOx/NiCrOx/Ag/AZO/ SnOx/ glass) multilayer films. The SnOx, NiCrOx, Ag and AZO in SnOx/NiCrOx/Ag/AZO/SnOx/glass function as dielectric, protection, infrared reflection and interfacial layer respectively. Microstructure, emissivity and optical properties of SnOx/NiCrOx/Ag /AZO/SnOx/glass and Ag /AZO/SnOx/glass (without protection layer on Ag) were measured and compared before and after heat treatment in this paper.

EXPERIMENTS

The glass to be deposited was ultrasonically cleaned in sequence with acetone, isopropyl alcohol and purified water. The cleaned glass was dried with nitrogen gas. The SnOx/NiCrOx/Ag/AZO/SnOx/glass samples were fabricated by in-line sputtering. Each layer in SnOx/NiCrOx/Ag/AZO/ SnOx/glass is 45, 3, 11, 6 and 45 nm in thickness respectively. The sputtering tool was pumped down below 10^{-5} torr as base pressure. Argon and oxygen with high purity and different ratio were applied as the process gas. The process pressure was kept at $3X10^{-3}$ torr and substrate temperature was controlled at room temperature. Inside and outside SnOx films were processed by the Sn target in pulsed DC mode and Argon/Oxygen reaction sputtering, The AZO and Ag films were produced with AZO and Ag target separately in DC mode. The NiCrOx films were deposited with Nickel/Chromium target in a pulsed DC mode and Argon/Oxygen reaction sputtering. Applied power density during sputtering is 1.8, 1.9, 2.2 and 1.0 watt respectively corresponding to SnOx, NiCrOx, Ag and AZO in processed multilayer films. A cross section of the prepared SnOx/NiCrOx/Ag/AZO/SnOx/glass was measured and shown in Figure 2.

(a)

SnOx(45nm)
NiCrOx(3nm)
Ag(11nm)
AZO(6nm)
SnOx(45nm)
glass

(b)

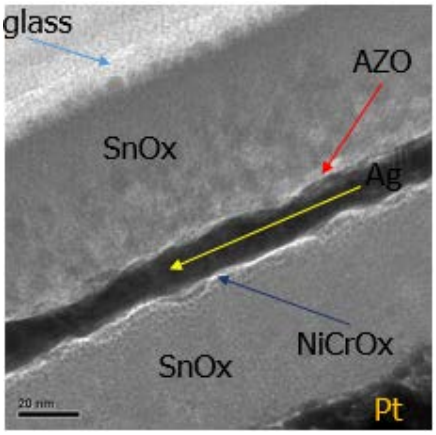


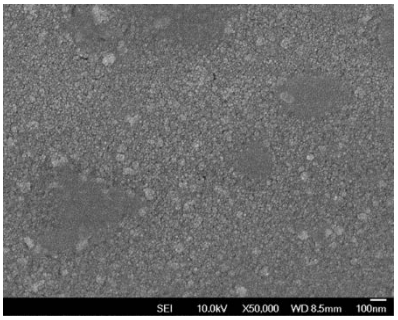
Figure 2. (a) Schematic and (b) produced diagram on cross section of SnOx/NiCrOx/Ag/AZO/ SnOx/glass.

The Ag/AZO/SnOx/glass samples (without protecting films on Ag) were also produced with the same recipe as Ag, AZO and SnOx films in SnOx/ NiCrOx/Ag/AZO/SnOx/glass. Part of Ag/AZO/ SnOx/glass and SnOx/NiCrOx/Ag/AZO/SnOx/glass samples were heated in vacuum at 500°C and for one hour. Microstructure, optical property and emissivity of the Ag/AZO/SnOx/glass and SnOx/NiCrOx/Ag/ AZO/SnOx/glass samples before and after heat treatment were measured and compared. Surface morphology, surface roughness, crystallinity, optical transmittance, optical reflectance and emissivity was measured by scanning electron microscope (HITACHI S-4800), atomic force microscope, X-ray diffractometer (Rigaku D/Max2500), UV/VIS/NIR spectrometer (PerkinElmer LAMBDA 750) and emissivity meter (AZ Technology TEMP 2000A).

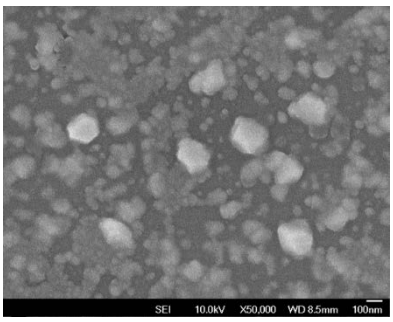
EXPERIMENTS RESULTS AND DISCUSSION

Scanning electron micrograph of Ag/AZO/ SnOx/glass and SnOx/NiCrOx/Ag/AZO/SnOx/glass samples before and after heat treatment was shown in Figure 3.

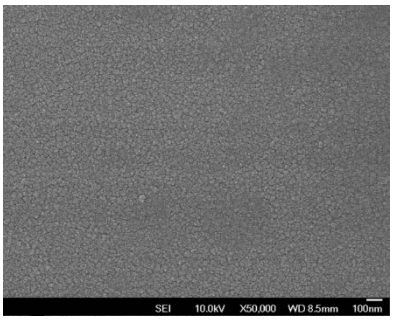
(a)



(b)



(c)



(d)

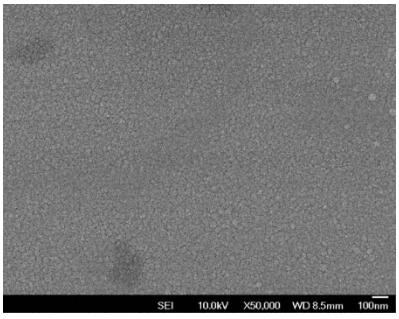


Figure 3. Scanning electron micrograph of (a) Ag/AZO/SnOx/glass before heat treatment, (b) Ag/AZO/SnOx/glass after heat treatment, (c) SnOx/NiCrOx/Ag/AZO/SnOx/glass before heat treatment and (d) SnOx/NiCrOx/Ag/AZO/SnOx/glass after heat treatment.

Heat treatment makes Ag/AZO/SnOx/glass apparent coalescence. Morphology of SnOx/NiCrOx/Ag/AZO/SnOx/glass is similar before and after heat treatment. Surface roughness Rrms of Ag/AZO/SnOx/glass and SnOx/NiCrOx/Ag/AZO/SnOx/glass samples measured by atomic force microscope was shown in table 1. Surface roughness Rrms of Ag/AZO/SnOx/ glass increases 11.22 times compared with that before heat treatment. Surface roughness Rrms of SnOx/ NiCrOx/Ag/AZO/SnOx/glass after heat treatment is similar to that before heat treatment. X-ray diffraction spectra of Ag/AZO/SnOx/glass and SnOx/NiCrOx/ Ag/AZO/SnOx/glass before and after heat treatment were shown in Figure 4.

Table 1. Surface roughness, average transmittance in the visible region (400~800 nm), average reflectance in the near infrared region (1100~2500 nm) and emittance of Ag/AZO/SnOx/glass and SnOx/NiCrOx/Ag/AZO/SnOx/glass samples before and after heat treatment.

Sample	Ag/AZO/SnOX/glass		SnOx/NiCrOX/Ag/AZO/SnOx/glass	
Heat Treatment	Before	After	Before	After
Surface Roughness Rrms (nm)	2.79	31.31	2.72	1.82
Average transmittance in visible (400~800 nm) region (%)	55.49	44.02	78.74	62.4
Average reflectance in near infrared (1100~2500 nm) region (%)	93.55	42.37	87.57	86.57
Emissivity	0.10	0.32	0.11	0.11

(a)

(b)

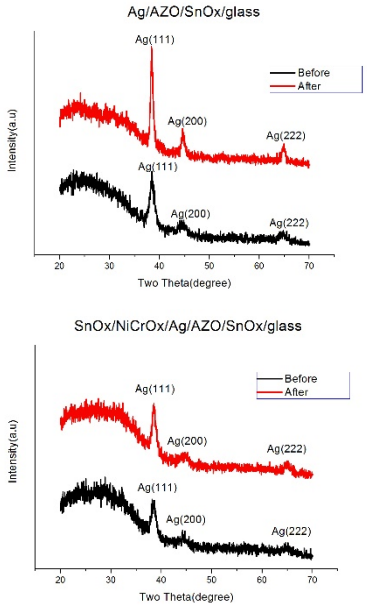
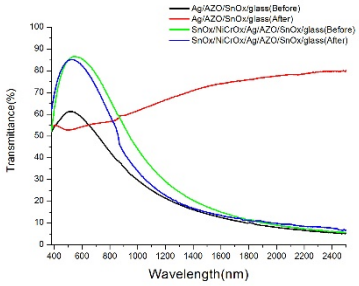


Figure 4. X-ray diffraction spectra of (a)

Ag/AZO/SnOx/glass and (b) SnOx/ NiCrOx/Ag/AZO/SnOx/glass before and after heat treatment.

Only Ag diffraction peaks were observed from Fig. 4. The full width at half maxima of diffraction peaks decrease for Ag/AZO/SnOx/glass after heat treatment, while those are similar for SnOx/ NiCrOx/Ag/AZO/SnOx/glass before and after heat treatment. Transmittance and reflection spectra of Ag/AZO/SnOx/glass and SnOx/NiCrOx/Ag/AZO/ SnOx/glass samples before and after heat treatment were shown in Figure 5.

(a)



(b)

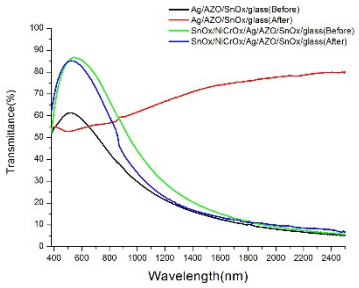


Figure 5. (a)Transmittance and (b) reflectance spectra of Ag/AZO/SnOx/glass and SnOx/NiCrOx/ Ag/AZO/SnOx/glass samples before and after heat treatment.

Groups of transmittance and reflectance curve shapes are similar except those corresponding to Ag/AZO/SnOx/glass samples after heat treatment. The average transmittance in the visible region (400~800 nm) and reflectance in the near infrared region (1100~2500 nm) were shown in table 1. The average reflectance in the near infrared region (1100~2500 nm) of Ag/AZO/SnOx/glass after heat treatment decreases apparently from 93.55 to 42.37 %. The measured emittance of Ag/AZO/SnOx/glass and SnOx/NiCrOx/Ag/AZO/SnOx/glass samples before and after heat treatment was also shown in table 1. All emittance values in table 1 are similar except that corresponding to heat treated Ag/AZO/SnOx/glass samples. The emittance of Ag/AZO/SnOx/glass sample increases from 0.10 to 0.32 after heat treatment.

Results on microstructure shown in Fig.3, Fig.4 and table 1 implies Ag/AZO/SnOx/glass alters its microstructure after heat treatment: Ag agglomeration occurred and surface roughness increased, which are similar to those reported by Choi et al. (Choi, K. H.et al, 1999). Microstructure change results in deteriorating emissivity for heated Ag/AZO/SnOx/ glass. However, microstructure of SnOx/NiCrOx/Ag/ AZO/SnOx/glass samples after heat treatment is similar to that before heat treatment. Two layers: SnOx/NiCrOx on Ag/AZO/SnOx/glass can effectively prevent Ag agglomeration. The microstructure-alteration phenomena explain SnOx/ NiCrOx/Ag/AZO/SnOx/ glass demonstrates similarly while Ag/AZO/SnOx/glass deteriates optical properties and emittance in Fig.5 and table 1 after heat treatment. Similar emissivity for SnOx/ NiCrOx/Ag/AZO/SnOx/glass before and after heat treatment explains SnOx/NiCrOx/Ag/AZO/SnOx/ glass is thermally stable applied for low-emissivity glass.

CONCLUSION

The Ag/AZO/SnOx/glass and SnOx/NiCrOx/ Ag/AZO/SnOx/glass samples were prepared by in-line sputtering. Part of the deposited Ag/AZO/ SnOx/glass and SnOx/NiCrOx/Ag/AZO/SnOx/glass samples were heated at 500°C and for 1 hr. After heat treatment, the optical and emissivity property of Ag/ AZO/SnOx/glass samples deteriates resulted from Ag agglomeration. Thermal stability of SnOx/NiCrOx/ Ag/AZO/SnOx/glass is relatively good. The microstructure, optical and emissivity properties of SnOx/NiCrOx/Ag/AZO/SnOx/glass after heat treatment are similar to those before heat treatment.

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用於低輻射玻璃的氧化錫/氧化鎳鉻/銀/氧化鋁鋅/氧化錫/玻璃多層膜其熱穩定性

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國家奈米元件實驗室

摘 要

低輻射玻璃是隔絕熱的玻璃，它在可見光範圍具高穿透且在紅外線範圍具高反射特性。以銀為基底的多層膜是目前市面上最常使用的低輻射玻璃材料。低輻射玻璃製造過程通常需要高溫處理例如彎曲或硬化過程。經加熱後材料的低輻射特性可能變差。氧化錫/氧化鎳鉻/銀/氧化鋁鋅/氧化錫/玻璃和銀/氧化鋁鋅/氧化錫/玻璃試片使用直線式連續濺鍍做出。這兩類試片再經500℃，1小時的熱處理。結果顯示氧化錫/氧化鎳鉻/銀/氧化鋁鋅/氧化錫/玻璃經熱處理後其微結構，光特性和低輻射係數並無明顯改變。但銀/氧化鋁鋅/氧化錫/玻璃試片經熱處理後其微結構，光特性改變，且低輻射係數從0.10升到0.32。氧化錫/氧化鎳鉻/銀/氧化鋁鋅/氧化錫/玻璃的外層氧化錫/氧化鎳鉻層可有效的防止銀層團聚改變。這篇文章對節能建築有貢獻。