Effects of Temperature on the Infrared Emission Performance of AZO Films

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Abstract With the decrease of global resources and environmental deterioration，energy saving and emission reduction have become a hot topic and Low-E glass with thermal insulation performance is becoming the research focus. To improve the thermal insulation performance of glass，the simplest and most effective method is plating low-emissivity coatings on the surface of them. . The Al doped ZnO (AZO) film is the most potential low-emissivity layer for Low-E glass，due to rich raw materials，high conductivity and high transparency and so on. Effects of temperature on the infrared emission performance of AZO films were researched and mechanisms of changes were analyzed in this study. The change of infrared emissivity of AZO film kept at a certain temperature for some time was studied firstly，and then the change of infrared emissivity in variable temperature environment was studied. 500 nm-thick AZO films were deposited on glass substrates at room temperature by direct current magnetron sputtering and then were put in muffle furnace for heat treatment. Films were kept at 100～400 ℃ for 1 h in air and then cooled to room temperature in the furnace. The phase of AZO films was analyzed by X-ray diffraction and the surface morphology was observed by scanning electron microscope. The resistivity was measured by four probe method and the infrared emissivity was measured using infrared emissivity measurement instrument. Visible spectrum was measured by visible spectrophotometer. The results showed that AZO film before and after annealed all show hexagonal wurtzite structure and (002) preferred orientation. With the annealing temperature rising to 300 ℃，the intensity of (002) diffraction peak increases，the full width of half maximum (FWHM) narrows down and grain size increases. With the increase of annealing temperature，the resistivity decreases firstly and then increase. The film annealed at 200 ℃ shows the lowest resistivity of $0.9\times10^{-3}\ \Omega\cdot$cm. The decrease of resistivity is attributed to the growth of grains. The film annealed at higher temperature in air will absorb oxygen，resulting in the decrease of resistivity. The change of the infrared emissivity with annealing temperature agrees to that of resistivity. The film annealed at 200 ℃ shows the lowest emissivity of 0.48. Infrared photons are strongly reflected by free electrons. When the resistivity is low and the concentration of free electrons is high，more infrared photons are reflected，the infrared radiation weakens，and the infrared emissivity decreases. The transmittance decreases firstly and then increases. It is the lowest at 200 ℃ but still up to 82%. This change is caused by the change of free electron concentration. Free electron strongly reflects visible light. The infrared emissivities of the films as-deposited and annealed at 200 ℃ were measured during the process of heating and cooling between room temperature and 350 ℃. The sample was fixed on the heated stage and its emissivity was recorded every 25 ℃. It was found that the infrared emissivity increases with the increase of temperature during the heating process，and decreases during the cooling process. After the whole process，the infrared emissivity of the AZO film increases.

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Introduction

Energy saving and emission reduction has become a hot topic which human concerned, due to the decrease of global oil resources and environmental deterioration. Significantly, building energy consumption accounts for about 30% of the total energy consumption. More significantly, heat loss through glass occupies a large proportion in building energy consumption. Therefore, it is very necessary to improve the thermal insulation performance of glass. The The simplest and most effective method is plating low-emissivity coatings on the surface of glass[1]. That glass is called as low-emissivity (Low-E) glass. There are two main categories of low-emissivity coatings: metal films and transparent conductive oxide (TCO) films[2-3]. The emissivity of metal films is low, but its transmittance is also low[4]. Compared with metal films, the transmittance of TCO films is higher. Among all kinds of TCO films, Al doped ZnO (AZO) films become the research focus due to nontoxicity, rich raw materials and low cost[5-6]. In this study, AZO films were deposited by DC magnetron sputtering. Effects of temperature on the emissivity were researched in detail.

1 Experimental detail

The AZO films were deposited on glass substrates by DC magnetron sputtering. AZO target (2 Wt% Al_2O_3) was used. The thickness was kept around 500 nm. After deposition, the AZO films were put in muffle furnace for heat treatment. Films were kept at 100～400 ℃ respectively for 1 h and then cooled to room temperature in the furnace.

The film thickness was examined using a surface profiler (Ambios, XP2). The phase was examined by X-ray powder diffraction (Philips X'Pert diffractometer). The surface morphology was observed with a scanning electron microscope (SEM) (JSM-6360, Japan). The resistivity was obtained by four-point probe method. The transmission was measured by UV-Vis spectrophotomtery (Shimadzu uv3150, Japan). The mean emissivity in 8～14 μm wavebands was measured with an infrared emissivity measurement instrument (ISTP IR-2, China) by adopting the reflection method[7].

2 Results and discussion

Fig. 1 shows X-ray diffraction (XRD) spectra of AZO films. All AZO films show hexagonal wurtzite structure and obvious (002) preferred orientation, which is a typical texture for AZO film[8-9]. With the annealing temperature rising to 300 ℃, the intensity of (002) diffraction peak increases, and the full width of half maximum (FWHM) narrows down. Whereas the intensity of (002) peak greatly decreases and the intensity of (102) diffraction peak obviously increases with the temperature further rising to 400 ℃. An appropriate increase of annealing temperature is beneficial to improve the crystalline quality. But if the annealing temperature is too high, the random thermal motion of atoms enhances greatly, which is not beneficial to the preferred orientation of the films.

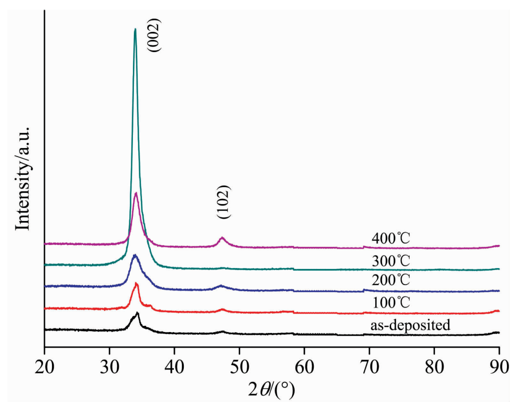

Fig. 1 XRD results of AZO films before and after annealed

Fig. 2 shows the surface morphologies of the AZO films. After annealed, the grain size becomes larger. During the process of annealing, film atoms will get more energy at higher temperature to migrate, leading to the growth of grains.

Fig. 3 shows the resistivity of AZO film. The resistivity firstly decreases and then increases with the increasing temperature, which is consistent with previous report[10-11]. The resistivity of the AZO film annealed at 200 ℃ is the lowest as 0.9×10^{-3} Ω·cm. The decrease of resistivity is attributed to the growth of grains. In addition, the film annealed in air will absorb oxygen, resulting in the reduction of oxygen vacancies and carrier concentration[12]. Therefore, the resistivity increases, when the annealing temperature is further increased.

Fig. 4 shows the mean emissivity of AZO film. The infrared emissivity decreases and then increases with the increasing temperature. It possesses the minimum value of 0.48 at 200 ℃. According to the results of XRD and SEM, the grains grow up after air annealing, which leads to the decrease of the scatter of infrared photons. Therefore, the interaction between the film and the infrared photon decreases, and the infrared emissivity decreases. When the annealing temperature increases further, the free electron concentration decreases. Reflection of electrons to infrared light decreases and the infrared emissivity increases.

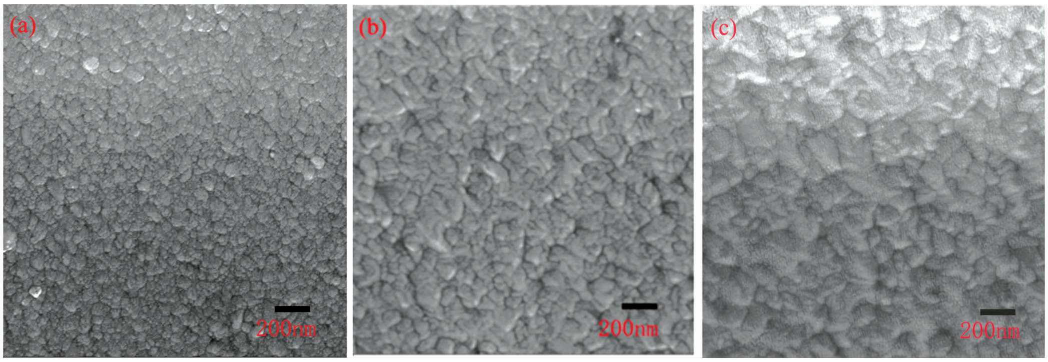

Fig. 2 SEM micrographs of the AZO films after annealing (a) as-deposited, (b) 200 ℃, (c) 300 ℃

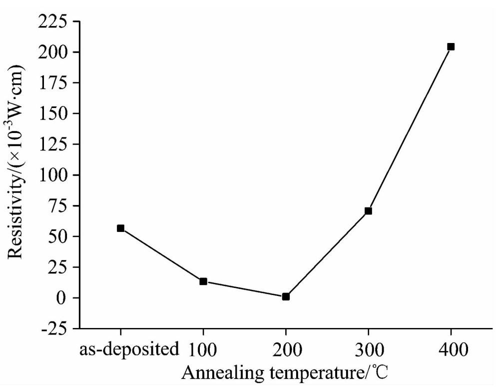

Fig. 3 Resistivity of the AZO film before and after annealed

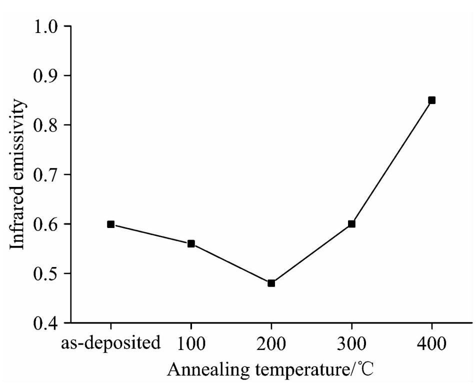

Fig. 4 Mean infrared emissivity of the film before and after annealed

Fig. 5 shows the emissivity of AZO film during the process of heating and cooling from room temperature to 350 ℃. The emissivity increases with the increasing measuring temperature. For the same film, its emissivity increases, after the whole process, of heating and cooling. With the increase of measuring temperature, relative vibration between different ions becomes stronger. It will cause a stronger production and absorption in the films for infrared photons. Therefore, the infrared emissivity increases during the heating process. The whole process of heating and cooling is equal to the annealing process. So the emissivity of the film after the whole process increases.

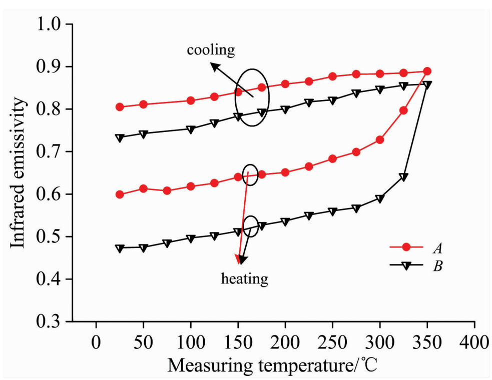

Fig. 5 Infrared emissivity of AZO film as a function of measuring temperature

(a): As-deposited; (b): Annealed at 200 ℃

Fig. 6 shows the transmittance spectra of AZO films and average transmittance in 400～800 nm wavebands. The average transmittance firstly decreases and then increases, with the lowest as 82% at 200 ℃. The decrease of transmittance of the films after annealed at 100 and 200 ℃ is conducive to more Al element substituting Zn-site. The increase of carrier concentration leads to the increase of photons scattering, resulting in the reduction of transmission. The scattering mechanism in AZO film is mainly ionic hybrid scattering. When the ion hybrid scattering is dominant, the increase of the carrier concentration will lead to the decrease of the transmission of light. When the annealing temperature is more than 200 ℃, the crystallinity of the film is greatly improved, the scattering of the photon is reduced, so the transmission of the film increases.

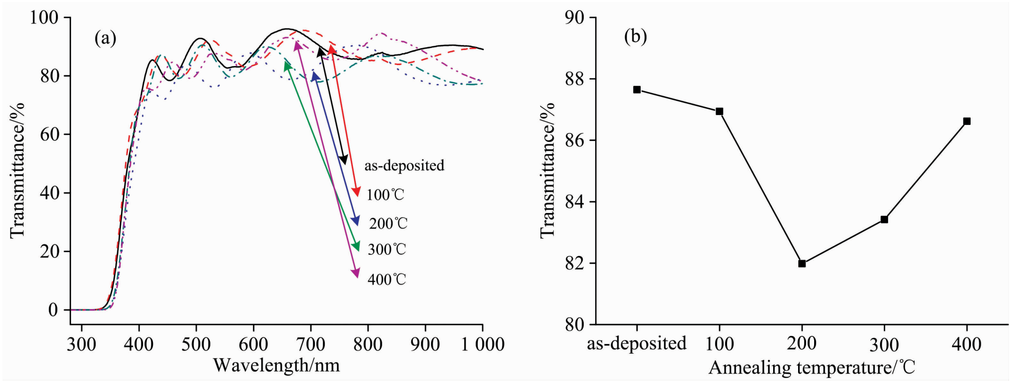

Fig. 6 Transmittance spectra of the AZO films (a) and the average transmittance (b)

3 Conclusions

(1) The AZO films deposited at room temperature and annealed in air show hexagonal wurtzite structure and (002) preferred orientation. The air annealing can promote grain growth and improve the crystallinity of the films.

(2) With the increase of annealing temperature, the resistivity and infrared emissivity of the AZO film decrease firstly and then increase, which is mainly due to the growth of grains and the changes of carrier concentration. The AZO film annealed at 200 ℃ shows the lowest resistivity (0.9×10^{-3} Ω · cm) and the lowest infrared emissivity (0.48).

(3) The infrared emissivity increases with the increase of measuring temperature from room temperature to 350 ℃, which is due to relative vibration between different ions in the AZO films.

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温度对 AZO 薄膜红外辐射性能的影响

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摘　要　随着全球资源的减少和环境的恶化，节能减排已成为人们关注的焦点，具有保温隔热功能的低辐射玻璃成为研究的热点。提高玻璃保温隔热性能最有效的方法就是在其表面涂覆低辐射率层。原材料丰富、导电性能好、可见光透过率高等优势使得 Al 掺杂 ZnO (AZO)薄膜成为最具潜力的低辐射率层。系统研究了温度对 AZO 薄膜红外辐射性能的影响，分析了变化机理。首先研究了在一定的温度下持续一段时间后，AZO 薄膜的红外比辐射率的变化情况。然后研究了在变温环境中红外比辐射率的变化情况。采用直流磁控溅射法在室温下玻璃基片上沉积 500 nm 厚的 AZO 薄膜，将薄膜放到马弗炉中进行热处理，在 100～400 ℃空气气氛下保温 1 h，随炉冷却。采用 X 射线衍射仪对 AZO 薄膜进行物相分析，采用扫描电子显微镜观察薄膜表面形貌变化。利用四探针测试法测量 AZO 薄膜的电阻率，采用红外比辐射率测试仪测试薄膜红外比辐射率，可见分光光度计测量可见光谱。测试的结果表明，薄膜热处理前后均为六角纤锌矿结构，(002)择优取向。300 ℃及以下热处理 1 h 后，(002)衍射峰增强，半高宽变窄，晶粒尺寸长大。随着热处理温度的升高，薄膜的电阻率先减小后增大，200 ℃热处理后的薄膜具有最小的电阻率(0.9×10^{-3} Ω·cm)。热处理温度升高，晶粒长大使得薄膜电阻率降低。热处理温度过高，薄膜会从空气中吸收氧，电阻率下降。薄膜的红外比辐射率变化趋势和电阻率的一致，在 200 ℃热处理后获得最小值(0.48)。自由电子对红外光子有较强的反射作用，当电阻率低，自由电子浓度高的时候，更多的红外光子被反射，红外辐射作用弱，红外比辐射率小。薄膜的可见光透过率随着热处理温度的升高先减小后增大，200 ℃热处理后的薄膜的可见光透过率最小，但仍高达 82%。这种变化是由于自由电子浓度变化引起的，自由电子对可见光有很强的反射作用。选取未热处理和 200 ℃热处理后的样品进行变温红外比辐射率的测量，将样品放在可加热的样品台上，位置固定，在室温到 350 ℃的升温和降温过程中每隔 25 ℃测量一次红外比辐射率，结果表明，在室温到 350 ℃的温度范围内，AZO 薄膜的红外比辐射率在升温过程中随着温度的上升而增大，在降温过程中减小，经过整个升、降温过程后，薄膜的红外比辐射率增大。

关键词　AZO 薄膜；直流磁控溅射；红外辐射性能；温度；透射光谱

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