直線式連續濺鍍製作氧化鋅摻鋁薄膜的非等向性應力效應

Anisotropic stress effect on aluminum doped zinc oxide films produced from in-line sputtering

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摘要

在薄膜太陽能電池工業中，需要大面積、量產的透明導電膜。本篇探討為符合上述製作條件：利用直線式連續濺鍍機，不同基板溫度下製作氧化鋅摻鋁薄膜。實驗結果發現當基板溫度高於 50°C 時，量測到薄膜電性質中的載子濃度或是移動率均有明顯的對時間不穩定性。甚至，X- 光繞射薄膜量測結果顯示當基板溫度高於 50°C 時，薄膜優選方向 (002) 繞射峰的高度隨著基板溫度越高而降低，與一般隨著基板溫度越高而升高不同。這兩項有趣的結果推測與直線式連續濺鍍機鍍製薄膜時產生非等向性應力有關。
關鍵詞：應力、直線式連續濺鍍機、氧化鋅摻鋁

Abstract

In this study, aluminum doped zinc oxide (AZO) films were prepared by in-line DC sputtering with different substrate temperatures in order to produce large area and high throughput transparent conductive oxide films applied in thin film solar cells. It was found that apparent time instability of carrier concentration and mobility for the AZO films prepared with substrate temperature higher than 50°C. Moreover, not only the measured X-ray diffraction intensity with respect to ZnO preferential (002) plane decreases but also for substrate temperature higher than 50°C. Both cases are believed to relate with anisotropic stress for the prepared AZO films produced during in-line sputtering process.
Keywords: stress, in-line sputtering, aluminum doped zinc oxide

1. Introduction

In decades, zinc oxide (ZnO) has been used in transparent electrodes for photovoltaic and flat panel displays, which attracts a great deal of attention[1]. Compared with the most generally used ITO transparent conducting film, Al-doped ZnO (AZO) is emerging as an alternative candidate for ITO thin films due to its low cost, nontoxic, easy to fabricate feature, the abundant raw material and good stability in plasma[2, 3]. Recently, the electrical conductivity of intrinsic ZnO is mainly attributed to oxygen vacancies and zinc interstitials[4]. Moreover, extrinsic impurities doping, such as group IIIA: aluminum, boron, gallium and indium[5, 6] and group VII A: fluorine[7] can increase the conductivity of ZnO further. However, chemical stability under hydrogen plasma which often exists in silicon thin film solar cell process makes ZnO a better candidate than indium tin oxide applied in solar cells industry[1].

Recently, much effort has been made in the processes of ZnO film productions, for example: chemical vapor deposition[8] and chemical spray[9]. However, most of the researches mainly focused on the dependence of transparent conductive properties of AZO film produced from batch instead of in-line type sputtering system. These study results can be directly applied on in-line sputter produced AZO films or not is what we are interested in. In-line sputtering tools can produce a large area and high throughput coating, to meet the expectation in the industry. Hong et al. pointed out in 2003 that aluminum doped zinc oxide films were produced by in line reactive mid-frequency sputtering with sputtering metal Zinc/Aluminum targets[6]. It is difficult to obtain the required uniform films' properties by the reactive sputtering due to its non-linear process characteristics. In this article, AZO films were produced by in-line DC sputtering with a sputtering ceramic AZO target. Anisotropic stress of thin films generated during in-line sputtering was found. Suzuki reported it may be ascribed to oblique incidence of the sputtered particles during the substrate entered and left the coating zone of the target[10]. The in-line sputtered film properties were corresponding to the process produced stress effect.

2. Experimental Procedure

Borosilicate glass prepared as coating substrate was ultrasonically cleaned with purified water for 5 min and acetone for 5 min sequentially twice. After that, the glass was final cleaned with purified water and dried with nitrogen gas. One in-line DC magnetron sputtering tool was used as the coating tool. The ceramic AZO target with ZnO/Al_2O_3= 98:2 wt% was applied. The target dimension was 95×20 cm^2. The power density was 1.58 W/cm^2 during sputtering. The process chamber was pumped down to 5×10^{-3} Pa as base pressure. The process pressure was 3×10^{-1} Pa and filled with pure Ar gas. Different substrate temperatures (room temperature, 50, 100, 150 and 200°C) were applied. The substrate was moved with a speed of 0.6 cm/sec during sputtering process.

Electrical and microstructure properties of the in-line sputtered AZO films with a thickness of about 500 nm were measured. Carrier concentration, mobility and electrical resistivity by hall measurement with van der Pauw method were measured at room temperature. The crystalline structure was determined by X-ray diffract meter at low grazing angle. To investigate the electrical stability variation as a function of time, the electrical properties of the as-prepared films and films stored for one month were both measured.

3. Results and Discussions

3.1 Results

The electric resistivities of AZO films prepared with different substrate temperatures were measured immediately (MI) and with one month storage (MWOMS) respectively after films production are shown in Fig.1. There is a big difference between films MI and MWOMS: the electrical resistivity is more than 6 times lower in the MI films than that of the MWOMS films at 100°C substrate temperature (as shown in Fig.1). The electrical resistivity of the MI films is about one time lower than that of the MWOMS films at 200°C substrate temperature. The electrical resistivity of AZO films is proportional to the product of carrier concentration and mobility. The measured carrier concentrations of MI films and MWOMS films varied with substrate temperatures. They are nearly the same at room temperature and 50°C; but they are apparently different at 100, 150 and 200°C. However, the measured mobility has similar behavior.

The X-ray diffraction spectra of AZO films prepared with different substrate temperatures are shown in Fig.2. Films prepared at all substrate temperatures exhibit a clear (002) preferential orientation as observed in Fig.2. The (002) peak intensity increases from room temperature to 50°C but that decreases from 50 to 200°C.

3.2 Discussions

Based on the measured electrical and microstructure properties, anisotropic stress was believed to exist in AZO films. Time instability of the electrical property—carrier concentration and mobility was observed for AZO films produced with substrate temperature higher than 50°C. Sputtering process produces stress between films and substrate with several reasons: thermal and/or epitaxial mismatch between the films, different substrate thermal coefficients and lattice parameters[11]. Anisotropic stress during in-line sputtering can be produced by oblique incidence of sputtered particles mentioned before[8]. In addition, the substrate moves in line direction parallel to target during sputtering for in-line tool. The deposited films have inertia corresponding to original films deposited position relative to the moving substrate. This situation is similar to passengers staying in the moving bus. The passengers correspond to the deposited films and the moving bus corresponds to original films on moving substrate. The inertia creates stress inside films which is only in substrate moving direction. The direction perpendicular to the substrate moving line does not have this inertia created stress for deposited films. The proposed inertia produced films stress is also anisotropic. The anisotropic films stress no matter created by oblique sputtered particles or the proposed films inertia is believed to distribute strongest at the films substrate interface due the physical parameters mismatch between films and substrate mentioned previously[11]. If sputtering is proceeded at high temperature, the films substrate interface stress will relax[11]. The in-line sputtered AZO films in this work start to relax stress from films bottom (films substrate interface) to films top during sputtering when substrate temperature is relatively high- 100°C or above in this work. The residual stress inside films after sputtering still gradually relaxes with time to a certain extent which changes the films defects with a certain amount. The proposed residual stress should have the most corresponding to AZO films prepared with 100°C substrate temperature in this work, because films substrate interface stress begins to relax during sputtering for this preparation recipe. The films reserve the residual stress most due the provided thermal energy from substrate is just enough to "trigger" the stress relaxation, but far away enough to relax stress completely. This mechanism may explain why both the measured carrier concentration and mobility decreases much. Therefore, the electrical resistivity for AZO films prepared with 100°C substrate temperature decreases a lot by comparing films MWOMS with MI shown in Fig. 1. The measured carrier concentration increases and mobility decreases by comparing films MWOMS with MI for AZO films prepared with 150°C substrate temperature. The product of the two parameters—the electrical resistivities are similar for AZO films prepared with 150°C substrate temperature by comparing films MWOMS with MI shown in Fig. 1.

Same anisotropic stress scenario can be applied in explaining X-ray data in Fig.2. The residual anisotropic stress inside AZO films prepared when substrate temperature is higher than 50°C degrades the films microstructure. The damage of the crystalline structure increases with the substrate temperature. That can be the reason why X-ray diffraction intensity corresponding to (002) plane starts to decrease when the AZO films prepared with substrate temperature higher than 50°C. Previous reports on sputtered AZO films indicate the (002) X-ray diffraction intensity increases with substrate temperature up to 200°C whatever DC[12] or RF[13] sputtering is used. It is reasonably explained as following: as the substrate temperature increased, more thermal energy is transferred from substrate to the produced films, which makes films good crystallization. The result difference between previous reports and ours is attributed to that instead of batch type process tool, in-line sputtering was used in this work and hence the above mentioned anisotropic stress effect appeared.

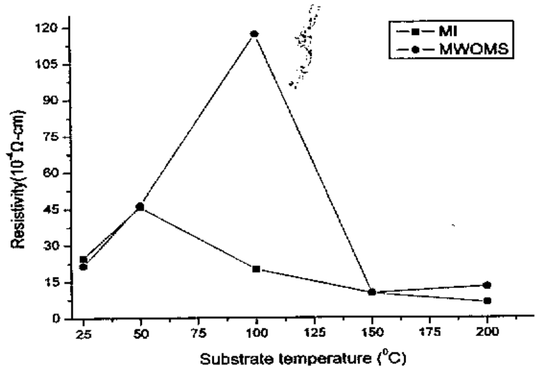

Fig.1.The electric resistivity of AZO films prepared with different substrate temperature was measured immediately (MI) and with one month storage (MWOMS) respectively after films production.

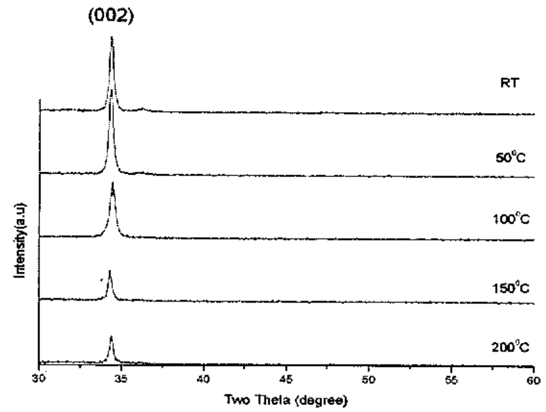

Fig.2. The X-ray diffraction spectra of AZO films prepared with different substrate temperature

4. Summary

The AZO films have been produced by using in-line DC sputtering with different substrate temperatures. Time instability of electrical properties and crystalline structure degradation for AZO films was found as the substrate temperature is higher than 50°C. Relaxation of films substrate interface stress produced during in-line sputtering process with high substrate temperature is the main reason. Anisotropic stress generated by films inertia corresponding to original films deposited position relative to the moving substrate during sputtering process by using in-line sputtering tool, was proposed.

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