

Influence of Atomic Hydrogen on Transparent Conducting Oxide During Hydrogenated Microcrystalline Si Preparation by PECVD*

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Abstract: The hydrogen plasma degradation of transparent conduction oxides (TCO) is studied for hydrogenated microcrystalline Si($\mu\text{c-Si:H}$) prepared by plasma enhanced chemical vapor deposition (PECVD). TCO films such as SnO_2 and SnO_2/ZnO bi-layer films were exposed to atomic H at various substrate temperatures and for various treatment times. A decrease in the transmittance due to reduction by atomic H was scarcely observed for SnO_2/ZnO bi-layer, while a decrease for SnO_2 was found to depend strongly on the substrate temperature. The resistivity of SnO_2 films decreases significantly when substrate temperature exceeds 150°C in H-plasma. However, H-plasma treatment has little impact on the resistivity of SnO_2/ZnO bi-layer film. The reason for the decrease in the transmittance is the appearance of metallic Sn on the surface, and under this condition no $\mu\text{c-Si:H}$ film is deposited. SnO_2/ZnO bi-layer is very effective for the suppression of the reduction of TCO during $\mu\text{c-Si:H}$ deposition. The performance of microcrystalline silicon solar cells fabricated on $\text{ZnO}/\text{SnO}_2/\text{glass}$ is also investigated.

Key words: TCO; hydrogenated microcrystalline silicon; hydrogen plasma degradation

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1 Introduction

TCO plays a key role in the fabrication of Si-based thin film solar cells. TCO material is used to provide a window for the incident illumination to the device and also serves as one of the electrodes of solar cell. SnO_2 -coated glass is widely used as the substrate for amorphous silicon solar cells. However, in case of hydrogenated microcrystalline Si($\mu\text{c-Si:H}$)-based solar cells^[1], ZnO coated glass has been used due to its better stability under H-plasma. In this case, high hydrogen dilution of silane is used to deposit microcrystalline Si. TCO coating is exposed to intense hydrogen plasma during the deposition of a microcrystalline p-layer, which is the first layer of a p-i-n solar cell. It was reported by Das *et al.*^[2] and Masuda *et al.*^[3] that under hydrogen plasma, the optical transmission as well as the surface of SnO_2 coated substrate

deteriorate due to its low chemical stability. However, no detailed studies on hydrogen plasma degradation have been made on ZnO films deposited by direct current (DC) magnetron sputtering^[4] or on deposited silicon film properties.

This paper addresses the development of SnO_2 and SnO_2/ZnO bi-layer films by DC-magnetron sputtering. SnO_2 and SnO_2/ZnO films were exposed in H-plasma at different substrate temperatures for various times. The optical properties, surface morphologies, and resistivities of these TCO films before and after H-plasma exposure were studied. Finally, a $\mu\text{c-Si:H}$ thin film solar cell was fabricated on $\text{ZnO}/\text{SnO}_2/\text{glass}$.

2 Experiments

ZnO films with thickness of 50nm were deposited on SnO_2 -coated glass by DC-magnetron sputtering at a substrate temperature $T_s = 300^\circ\text{C}$,

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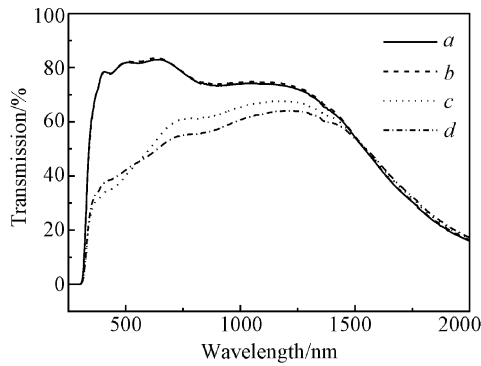


Fig. 1 Optical transmission spectra of SnO_2 film. Curve *a*: As deposited and after H-plasma exposure; Curve *b*: Exposure for 5min at 150°C ; Curve *c*: Exposure for 5min at 200°C ; Curve *d*: Exposure for 1min at 300°C

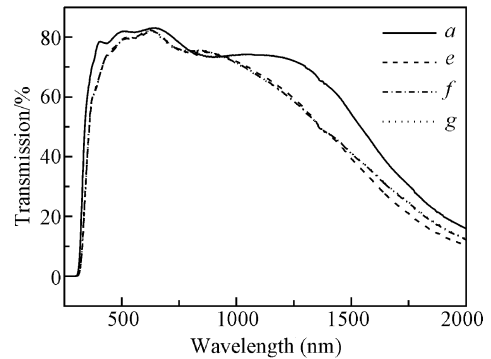


Fig. 2 Optical transmission spectra of SnO_2 film as deposited (Curve *a*), SnO_2/ZnO bi-layer film as deposited (Curve *e*), and SnO_2/ZnO bi-layer film after H-plasma exposure for 5min at 300°C (Curve *f*) and for 10min at 300°C (Curve *g*)

DC voltage $V_{\text{DC}} = 250\text{V}$, and pressure 0.5Pa . The SnO_2 and SnO_2/ZnO films were exposed under hydrogen plasma with the conditions of 50W RF-power, 130Pa chamber pressure, and 200sccm H_2 flow, where the substrate temperatures and exposure times were changed. Film characterizations were performed before and after the plasma exposure. The optical transmissions of the TCO films were measured with a UV spectrophotometer, and the surface morphologies were studied by scanning electron microscopy (SEM). The resistivities of the SnO_2 and SnO_2/ZnO films before and after H-plasma exposure were tested with a four-point probe.

Simple microcrystalline solar cells were fabricated in a multichamber PECVD system with diode type parallel plate reactors decomposing different gas mixtures by plasma on SnO_2/ZnO film. The p-i-n structure was glass/ $\text{SnO}_2/\text{ZnO}/\text{p-}\mu\text{c-Si:H}/\text{i-}\mu\text{c-Si:H}/\text{n-}\mu\text{c-Si:H}/\text{Al}$. The performances of the solar cells were studied from current-voltage characteristics, measured under AM 1.5 illumination by a source solar simulator.

3 Results and discussion

3.1 Optical transmission

Figures 1 and 2 show the optical transmission spectra of the single layer SnO_2 and bi-layer SnO_2/ZnO films before and after hydrogen plasma exposure, respectively. In all the cases, the optical transmission is high over a wider range of wavelengths for both single-layer SnO_2 (curve *a* of Fig. 1) and SnO_2/ZnO bi-layer (curve *e* of Fig. 2)

before H-plasma exposure. With thin ZnO film, the transmission in the range of visible light has little change. In Fig. 1, curve *b* shows the optical transmission of SnO_2 film after 5min hydrogen plasma exposure at 150°C , whereas curve *c* shows the transmission after 5min H-plasma exposure at 200°C and curve *d* shows the transmission after 1min H-plasma exposure at 300°C . At 150°C , the SnO_2 film is stable enough during H-plasma exposure and the optical transmission does not change at all. However when the substrate temperature is higher than 150°C , the transmission in the visible range decreases drastically. In the case of SnO_2/ZnO bi-layer film (shown in Fig. 2), ZnO coating induces a decrease in the transmission in the infrared region, but the change in transmission is very small, and after the H-plasma exposure there is a slight increase in infrared transmission. This may be beneficial for its application in solar cells as a window layer.

3.2 Surface morphology

Figures 3 (a) and (b) show the surface morphologies of SnO_2 films before and after H-plasma exposure, respectively. After 1min of plasma exposure, the SEM of hydrogen plasma-exposed SnO_2 changed. Grains with size $\sim 80\text{nm}$ are observed in the plasma-degraded SnO_2 film, and the grains display spherical character. Meanwhile, gray powder appeared on the surface of the glass. The reason may be that under hydrogen plasma, H atoms react with lattice oxygen atoms and metallic Sn is presented.

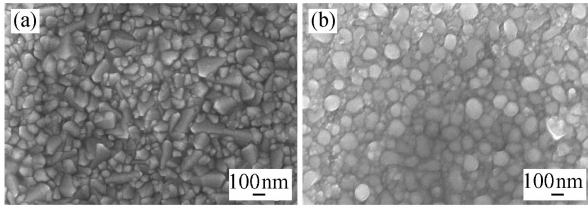


Fig. 3 Surface morphology of SnO₂ film (a) Before H-plasma exposure; (b) After 1min H-plasma exposure at 300°C

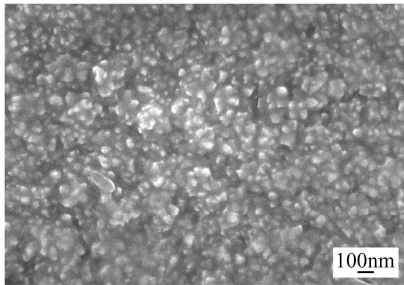


Fig. 4 Surface morphology of SnO₂/ZnO bi-layer film after 10min H-plasma exposure at 300°C

Figure 4 shows the surface morphology of SnO₂/ZnO bi-layer film after H-plasma exposure. Compared with the surface morphology of as-deposited ZnO film (not shown here), ZnO film does not degrade under hydrogen plasma, because a thin ZnO layer acts as a protective layer on SnO₂ surfaces, notwithstanding thickness of 50nm only. This bi-layer film can be exposed to H-plasma without any major change in optical transmission. The different durability of SnO₂ and ZnO to H-plasma is due to the different oxidizabilities of Sn and Zn ions, the former of which is higher than the latter.

3.3 Electric properties

Table 1 shows the resistivities of SnO₂ and SnO₂/ZnO bi-layer films before and after H-plasma exposure. For SnO₂ films, after 5min H-plasma exposure at 150°C, the resistivity becomes less than that of the deposited film, but remains on the same order of magnitude; When the temperature increases, the resistivity decreases sharply. This is

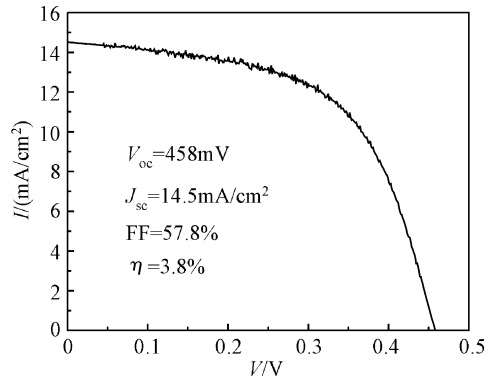


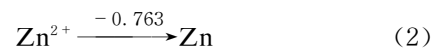
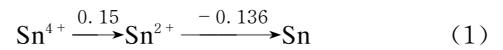
Fig. 5 *I-V* characteristics of hydrogenated microcrystalline Si thin film solar cells

caused by the deoxidization of Sn from the SnO₂ structure. For SnO₂/ZnO bi-layer films, H-plasma exposure has little influence on the resistivities of the films, and the decreasing of resistivities is caused by annealing at different substrate temperatures.

Simple single junction solar cells with the structure p-μc-Si:H/i-μc-Si:H/n-μc-Si:H/Al have been fabricated on glass/SnO₂/ZnO substrates. The *I-V* characteristics of this microcrystalline silicon based cells are shown in Fig. 5, and an efficiency of 3.8% is obtained. Das *et al.* [5] demonstrated that cells prepared on SnO₂-coated glass substrate have a low efficiency value. This is due to the degradation of SnO₂ film under high hydrogen plasma, which is essential for the fabrication of a p-μc-Si:H layer.

3.4 Discussion

The reasons that ZnO film is more stable than SnO₂ film in H-plasma can be explained by the difference of standard electrode electrical potential between metal Zn and Sn:



Equations (1) and (2) show the standard electrode potential electrical potential of metal Sn and

Table 1 Resistivities of SnO₂, SnO₂/ZnO bi-layer films before and after H-plasma exposure Ω · cm

	As deposited	150°C 5min	200°C 5min	300°C		
				1min	5min	10min
SnO ₂	7.31 × 10 ⁻⁴	6.42 × 10 ⁻⁴	4.75 × 10 ⁻⁵	7.68 × 10 ⁻⁶	/	/
SnO ₂ /ZnO	5.78 × 10 ⁻⁴	5.74 × 10 ⁻⁴	5.67 × 10 ⁻⁴	/	5.57 × 10 ⁻⁴	5.56 × 10 ⁻⁴

Zn. Although this value is measured in liquid solution, we can obtain that the electrical potential of Sn^{4+} is much higher than Zn^{2+} iron in the same state. This means that in films ZnO is more stable than SnO_2 under H-plasma condition, and the latter may react as follows:



Thus, the optical transmission of SnO_2 films decreases drastically under H-plasma of the p layer and the maximum part of incident light will be absorbed inside the TCO, i. e. effective light absorption in the active layer is reduced. SnO_2/ZnO structure is stable enough in H-plasma and can be applied in microcrystalline silicon solar cells.

4 Conclusions

SnO_2 and ZnO coated SnO_2 were exposed to atomic H for various substrate temperatures and exposure times. It was found that although transmission in the near infrared region is lower in the case of SnO_2/ZnO bi-layer, the degradation of SnO_2/ZnO bi-layer film is not significant after H-plasma exposure for 10min at 300°C , and SnO_2 is easily reduced to metallic Sn by atomic H, depending on the substrate temperature and exposure

time, which causes a decrease in the transmission and resistivity for SnO_2 . Using this SnO_2/ZnO bi-layer, microcrystalline silicon solar cells with efficiency of 3.8% were fabricated. All this demonstrates that ZnO films deposited on SnO_2 films are very stable in H-plasma and can be used in the fabrication of microcrystalline silicon solar cells.

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PECVD 沉积微晶硅薄膜过程中氢原子对透明导电膜的影响*

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摘要: 研究了等离子体放电过程中氢原子对单层 SnO_2 和 SnO_2/ZnO 双层透明导电膜的影响. 发现当衬底温度超过 150°C , H 等离子体处理使 SnO_2 薄膜的透光率显著降低. 当在 SnO_2 薄膜表面沉积一层 ZnO 时, 即使 ZnO 膜的厚度为 50nm, 也可有效地抑制 H 原子对 SnO_2 的还原效应, 并在 SnO_2/ZnO 双层膜上制备了转换效率为 3.8% 的微晶硅薄膜太阳能电池.

关键词: 透明导电氧化物; 氢化微晶硅; H 等离子体退化

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