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Review

Characterization of ZnO:Ga transparent contact electrodes for microcrystalline silicon thin film solar cells

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ABSTRACT

Gallium-doped zinc oxide (ZnO:Ga) thin films are of interest to the semiconductor industry as transparent conductive surfaces and as transparent contact electrode layers for applications such as microcrystalline silicon (μc-Si) thin film solar cells. Physical vapor deposition (PVD) via sputtering is commonly used to produce thin films such as ZnO:Ga, but film quality and characteristics depend significantly on the PVD processing parameters. For use as contact electrode layers in μc-Si thin film solar cells, this study investigates some of the important changes of ZnO:Ga thin films that result from varying DC magnetron PVD sputtering parameters, specifically the working power (500, 1200, and 1900 w), process gas (Ar, Ar/O_2=50/0.2 sccm) and working pressure (0.74 and 1.06 Pa). Process temperature is held at 200 °C because thin film solar cells are damaged above 200 °C. Adding O_2 to the Ar carrier gas improved transmittance but the resistivity suffered. However, high-sputtering power solved the resistivity problem. Additionally, the effects of the produced ZnO:Ga material when applied as multi-layer front and back layer electrodes to μc-Si thin film solar cells is evaluated in terms of open-circuit voltage (ΔV_{OC}), short-circuit current density (ΔJ_{SC}), fill factor (ΔFF) and efficiency ($\Delta\eta$) of the cells.

Contents

1. Introduction

Transparent conductors have become a basic material of modern society. They are found primarily in optoelectronic applications such as light emitting diodes (LED), solid-state lighting, flat panel liquid crystal displays (LCD) and solar cells. With mounting consumer pressure for larger video displays, energy-efficient lighting and alternative energy sources, the worldwide demand for transparent conductive films is increasing rapidly.

Transparent conductive materials are simultaneously optically transparent and electrically conductive. In 1907 Baedeker discovered that thin CdO films possess such characteristics [1]. Further work revealed that concurrent transparency and conductivity are not uncommon in metal oxides. In consequence, the majority of contemporary transparent conductors are based on metal oxides. The electrical conductivity and optical transparency of these materials depend on the nature, number and atomic arrangements of metal cations in the oxide structure and on the presence of intrinsic or intentionally introduced defects. Conductivity is due to doping either by oxygen vacancies or by extrinsic dopants. In the absence of doping, these oxides become good insulators. Al-doped zinc oxide (ZnO:Al, AZO), tin-doped indium oxide (In_2O_3:Sn, ITO) and antimony- or fluorine-doped tin

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oxide (SnO_2:Sb, SnO_2:F, ATO and FTO) are at present the most utilized transparent conductive oxides (TCO) TCO thin films in modern technology [2].

In fact, the industry standard TCO is ITO, with low resistivity ($\sim 10^{-4}\,\Omega\,cm$) and good transmittance ($>80\%$). The primary disadvantage of ITO is the high price of indium, which is a little less rare than the metal silver. Largely as a consequence of increased worldwide LCD production, demand for indium has risen rapidly, with an approximately 10-fold increase in price over the last decade (US$94/kg in 2002, US$700–$1000/kg in 2005–2007) [3]. Increasingly high indium prices are helping to drive the search for alternative TCO materials. In addition to economic issues, ITO suffers from limited optical tunability and poor mechanical flexibility, e.g. it cracks when used in the current generation of touch screen displays and is likely to do so in next-generation rollable displays.

In consequence of price and performance issues, a number of promising alternative materials are being investigated. Transparent conductors made from carbon-based graphene nanotubes are attracting significant attention. For example, Hu et al. recently reported that transparent nanotube electrodes and transparent graphene electrodes outperform contemporary alternatives in several key categories [4]. Transparent conductive polymers (TCP) are less conductive than TCO and absorb significant visible and IR spectrum, but TCP can be made into flexible films well suited to flexible electronic devices. Nevertheless, the present need of the industry is an inexpensive substitute for indium in the already successful metallic oxides. Moreover, a successful alternative TCO film material must be compatible with high-throughput large-area processing. Further, the material must be well-characterized for various processing methods because small processing changes can result in large changes in product quality. It is also desired that processing temperatures be minimized, since higher temperatures cause degradation of the silicon substrates used in thin film solar cells.

ZnO, commonly found in baby powder and sun tan oil, is an inexpensive, environmentally friendly material that is well-characterized for a wide variety of industrial applications. Compared with SnO_2- or In_2O_3-based films, ZnO-based TCO films have superior electro-optical properties and are more durable when subjected to hydrogen plasma treatment [5–7]. Al and Ga dopants enhance free-carrier generation in ZnO films [8–11]. Thus, AZO is one of the alternative TCO materials under current study. Similar to AZO, gallium-doped zinc oxide (ZnO:Ga) films have been receiving attention due to low material costs in conjunction with relatively low deposition temperatures during fabrication [12,13].

Hydrogenated microcrystalline silicon (μc-Si) thin film is considered as one of the most promising materials for silicon-based thin film solar cells because of superior performance stability and relatively higher conversion efficiency relative to amorphous silicon solar cells. Therefore, the question of how best and most inexpensively to fabricate high efficiency μc-Si solar cells has becomes an important issue [14,15]. A key aspect of this issue is optimum design and fabrication of TCO electrodes for high efficiency single μc-Si solar cells. In consequence, this article considers ZnO:Ga film as transparent contact electrode material on μc-Si thin film solar cells. In particular, this study characterizes some of the important changes to a ZnO:Ga thin film that result from varying DC magnetron PVD sputtering parameters, specifically the working power (500, 1200, and 1900 w), process gas (Ar, Ar/O_2=50/0.2 sccm) and working pressure (0.74 and 1.06 Pa). Process temperature is held at 200 °C because thin film solar cells are damaged above 200 °C.

The paper is organized as follows: after an initial introduction, we present the experimental setup and discuss the conditions that are varied during the DC magnetron sputtering fabrication process. Experimental results are then presented. The effects of the varied parameters on the electrical, optical and structural properties of ZnO:Ga films are analyzed and discussed. Additionally, this study also performs experimental evaluation of SnO_2:F/ZnO:Ga bi-layer front contact electrodes and ZnO:Ga/Ag back reflector contact electrodes with regard to the performance of the fabricated μc-Si thin film solar cells. Finally, the concluding section summarizes the present work and offers a brief view of our planned future study.

2. Experimental

ZnO:Ga films were deposited on glass substrates by commercial DC magnetron sputtering system using a ceramic oxide target (0.6 wt% Ga_2O_3). The glass substrates were ultrasonically cleaned using detergent and deionized water, then dried by blown nitrogen. A series of ZnO:Ga films with a thickness of 100 ± 10 nm were prepared at 200 °C. Film thickness was measured by a spectroscopic ellipsometer (GES5E CCD Type, Sopra, France). During film deposition, two system gas pressures were used, 0.74 and 1.06 Pa. To investigate the effects of oxygen species on the film properties, the ambient gas of the PVD system was varied between two alternate states, one condition being pure Ar, the other being a mixture of $Ar+O_2$ (Ar/O_2=50/0.2 sccm). Different deposition rates of ZnO:Ga films were created by controlling the deposition power at 500, 1200, and 1900 W.

μc-Si thin film solar cells were fabricated by plasma enhanced chemical vapor deposition (PECVD) using a conventional 27.12 MHz plasma CVD system. The pin layers of the μc-Si thin film solar cells were fabricated by PECVD, but the TCO layer was fabricated by sputtering PVD. SiH_4, H_2, B_2H_6, CH_4, and PH_3 were used as gas sources. Commercially prepared textured glass/SnO_2:F was used as the substrate for a ZnO:Ga layer that was deposited as described above. Solar cells were then grown on the SnO_2:F / ZnO:Ga coated glass substrate with a p–i–n structure as: glass/TCO/p–μc-Si:H/i–μc-Si:H/n–μc-Si:H/TCO/Ag. Under illumination, the *I–V* properties and the electrical properties of the produced solar cells were measured by an AM 1.5 G double beam Solar simulator (YSS-50A, Yamashita Denso) and characterized by four-point probe and Hall effect measurement in the van der Pauw configuration (HL 550PC, Bio-rad) at room temperature. X-ray diffraction (XRD) patterns were obtained by 40 kV-20 mA CuK_α radiation (UltimaIV, Rigaku). Optical transmission of the films was measured using a UV–visible spectrophotometer (UV-4100, Hitachi).

3. Results and discussion

Resistivity and deposition rate as a function of deposition power for ZnO:Ga thin films deposited at 200 °C can be seen for Ar-only ambient in Fig. 1 (a) and $Ar+O_2$ ambient in Fig. 1 (b). Clearly, the deposition rate increases monotonically and identically from 4 to 18 Å/s as the deposition power increases from 500 to 1900 W in both figures, which is to say that the tested gas pressures and gas mixtures have no significant effect on the deposition rate. Specifically, the deposition power directly refers to the number of atoms sputtered from the target. For higher sputtering power, the sputtered species get a higher energy that contributes to the film growth. These higher energy particles have high-surface mobility and therefore, a higher growing process at the surface takes place [16–18]. With regard to resistivity, the films fabricated in Ar ambient at 1.06 Pa show little resistivity variance with increasing sputtering power, remaining almost