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Transition metal oxide window layer in thin film amorphous silicon solar cells

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ABSTRACT

Pin-type hydrogenated amorphous silicon solar cells have been fabricated by replacing state of the art silicon based window layer with more transparent transition metal oxide (TMO) materials. Three kinds of TMOs: vanadium oxide, tungsten oxide, and molybdenum oxide (MoO_x) were comparatively investigated to reveal the design principles of metal oxide window layers. It was found that MoO_x exhibited the best performance due to its higher work function property compared to other materials. In addition, the band alignment between MoO_x and amorphous Si controls the series resistance, which was verified through compositional variation of MoO_x thin films. The design principles of TMO window layer in amorphous Si solar cells are summarized as follows: A wide optical bandgap larger than 3.0 eV, a high work function larger than 5.2 eV, and a band alignment condition rendering efficient hole collection from amorphous Si absorber layer.

1. Introduction

Superstrate hydrogenated amorphous silicon (*a-Si*:H) solar cell, with an intrinsic layer sandwiched between *p*- and *n*-doped layers, is one of the main future options for cost-effective solar cells, which remains attractive in view of a variety of implementation in photovoltaic field [1,2]. Traditionally, a *p*-type window layer is essential to sustain built-in potential with rear n layer. Boron-doped amorphous silicon carbide (*p-a*-SiC) [3] and boron-doped microcrystalline silicon (*p-uc*-Si) [4] films were widely used as window layer of *a-Si*:H based solar cells. Recently, hydrogenated silicon oxide (*p-nc*-SiO_x) has been studied [5]. However, the parasitic absorption and poor doping capability of *a*-Si:H based window layers restrict the overall device performance [6,7], and the design and improvement in the optical and electrical properties of the window layer in *pin*-type *a-Si*:H solar cells are necessary to further enhance conversion efficiency. Thermally evaporated transition metal oxides (TMOs) are promising to replace state of the art window layer materials due to wide optical bandgap (E_{opt}), high work function (WF), and tunable *i-a*-Si:H/TMO interface. Furthermore, the process control is simpler than conventional plasma enhanced chemical vapor deposition. Recently, tungsten oxide (WO_x) and molybdenum oxide (MoO_x) have been demonstrated as window layer of *pin*-type *a-Si*:H based solar cells with performance enhancement compared to reference cells with *p-a*-SiC window layer [8,9]. In this paper, we investigate the design principles of TMO window layer in *a*-Si:H solar cells via comparative investigation of various TMO materials. In addition, the influence of band alignment between TMO and amorphous absorber layer is investigated from compositional variation of TMO thin films.

2. Experiment

Asahi U-type glass (glass/SnO_2) was used as substrate to deposit devices. Vanadium oxide (V_2O_x), WO_x, and MoO_x films were deposited by a thermal evaporator under a vacuum of 2.7×10^{-4} Pa with V_2O_5 source (Aldrich, 99.9%), $WO_{2.9}$ source (Alfa Aesar, 99.99%) and MoO_3 source (Alfa Aesar, 99.5%), respectively. The substrate temperature was kept constant at 20 °C. The thickness of the film was measured by an in situ quartz monitor, which is calibrated by spectroscopic ellipsometry (SE). A two-chamber system was used for fabricating *a*-Si:H solar cells, which consists of a photo-assisted chemical vapor deposition chamber for the *p*- and *n*-layers, an plasma enhanced chemical vapor deposition chamber for the intrinsic layer. The fabricated devices have a structure of glass/SnO_2/TMO (10 nm)/*i-a*-Si (500 nm)/*n-a*-Si (40 nm)/Al, and the cell area was 0.092 cm^2. 10-nm-thickness was the optimized thickness for the MoO_x window layer to realize best device performances, and additional scaling in MoO_x leads to a slight enhancement in photocurrent-generation with a degraded internal electric field [9]. These trends would be similar for other TMO materials, and the optimal thickness for each material can be different. However, we have compared the performances of different TCOs at a fixed thickness of 10 nm, which is the thickness condition in conventional *p-a*-SiC. To understand the essential criteria for TMO window layer and dependence of device performances on material properties, four kinds of substrates were prepared to fabricate devices: glass/SnO_2, glass/SnO_2/V_2O_x, glass/SnO_2/WO_x, and glass/SnO_2/MoO_x. All the samples have air exposure

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time around 1 min to control the influence of air contamination [10]. The detailed deposition conditions appeared in Ref. [11].

TMO films were grown on bare c-Si wafer for X-ray and ultraviolet photoemission spectroscopy (XPS, UPS) measurement, and on Corning 7059 glass for the σ_D and transmittance measurements. XPS and UPS study were performed using a Sigma probe system under an ultra high vacuum system (10^{-8} Pa) with Mg Ka X-ray source (1253.6 eV) and a He I (21.2 eV) discharge lamp. SE was performed to characterize the optical bandgap and refractive indices of the films (UVISEL, Jobin Yvon). Coplanar gap Al electrodes were deposited on the TMO films by a thermal evaporator to measure σ_D and active energy E_a, where the σ_D values were measured at different temperatures and the E_a was extracted from the slope of the Arrhenius plot. Photocurrent densities versus voltage (J–V) measurements were performed under AM 1.5, 100 mW/cm^2 irradiation using a Keithley 2400 source meter. A constant energy spectrophotometer (YQ-25-MV, JASCO) was used for external quantum efficiency (EQE) measurements.

3. Results and discussion

The photo J–V characteristics of the devices with TMO window layers are shown in Fig. 1. For the devices (glass/SnO_2/i/n/Al) without window layer the work function difference between SnO_2 and n-a-Si (around 0.6–0.7 eV) produces internal electric field, and thus produces photovoltaic conversion with the efficiency around 3.0% with open circuit voltage (V_{oc}) of 0.39 V and fill factor (FF) of 0.61. Inserting a TMO window layer between the SnO_2 and intrinsic layer results in increased device parameters, and the differences in parameters have close relationship with the optical bandgap and electronic band alignment of TMO films. For devices with WO_x and MoO_x window layer, the EQEs increase significantly at short wavelength region compared to other type of devices as shown in Fig. 1(b), which is consistent with the wide optical bandgap larger than 3.0 eV compared to that of V_2O_x based on the SE measurement, and the estimated bandgaps are 3.35, 3.25, and 2.3 eV for WO_x, MoO_x, and V_2O_x, respectively.

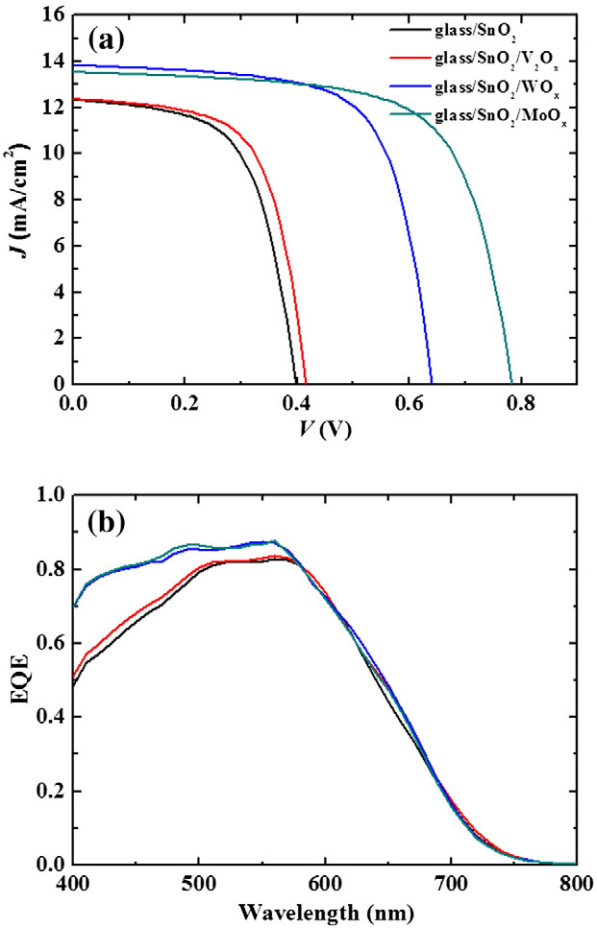

Fig. 1. Device performances for solar cells with different TMO window layer materials (a) photo J–V and (b) EQE.

The V_{oc} of the solar cell without TMO layer is only 0.39 V, and increases to 0.42, 0.64 and 0.78 V for the cell with a 10-nm-thick V_2O_x, WO_x, and MoO_x window layer, respectively. One reason for the difference in V_{oc} is related to the WF of TMO materials. According to the UPS analyses, WF of V_2O_x, WO_x, and MoO_x was found to be 4.7, 4.9, and 5.35 eV, respectively. The other reason of the differences in V_{oc} is attributed to the carrier recombination at TMO/i-a-Si interface, which implies the reduction of the electrons and holes quasi-Fermi level separation. The values of V_{oc} from the solar cell with V_2O_x and that with WO_x show larger difference than that expected from the difference in WF. This implies that the V_2O_x/i-a-Si interface contains larger interface states density than WO_x/i-a-Si interface in our interface forming condition (thermal evaporation at room temperature). The degradation of short wavelength EQE is related to the defect density near the window/i-a-Si interface, because most of photo-generation occurs in this region. The additional reason of the small short wavelength EQE in the solar cell with V_2O_x shown in Fig. 1(b) may be due to a possible larger interface state density. Similarly, the device without window layer (glass/SnO_2/i/n/Al) shows smaller EQE at 400 nm and smaller V_{oc} compared to those with WO_x or MoO_x window layers, which implies that the interface recombination at the SnO_2/i-a-Si interface significantly contributes to collection losses and narrowing the quasi-Fermi level separation.

The refractive indices of SnO_2, WO_x, and MoO_x are measured to be almost constant in visible range with values around 2.0, 2.1, and 2.3, respectively. In addition, the refractive index of V_2O_x is reported to be in the range from 2.2 to 2.8 in the visible range [12]. These implies that the insertion of TMO's between SnO_2 and i-a-Si:H can slightly reduce the optical reflectance, because the refractive index values of TMO's are between that of SnO_2 and that of i-a-Si:H (around 4). This again confirms that the short wavelength EQE degradation in V_2O_x applied solar cells is due to the electronic effect, and slight differences with SnO_2/i-a-Si:H structure can be explained by the optical effect.

For materials as window layers of pin-type a-Si:H solar cells, an optical bandgap larger than 3.0 eV is necessary to realize near zero parasitic absorption (transparent to visible light) because only the photon energy $h\nu > E_g$ can generate carrier (where h is the Planck's constant, $\nu = c / \lambda$ with c the speed of light and λ the wavelength, and E_g is the energy gap of the window layer considered). At the same time, a high WF is essential to sustain high built-in potential and obtain a high V_{oc} as shown in the band diagram of Fig. 2. The photo-generated holes are collected via recombination processes at the i-a-Si:H/TMO interface,

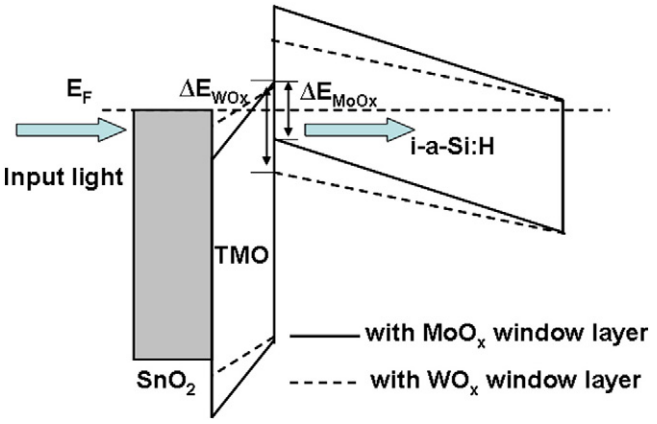

Fig. 2. Band diagram of SnO_2/TMO/i-a-Si:H/n-a-Si structure.