



Low work function intermetallic thin film as a back surface field material for hybrid solar cells

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ABSTRACT

In this study, MgNd intermetallic is deposited as a thin film using magnetron sputtering. Ultraviolet photoelectron spectroscopy (UPS) is employed to determine the work function of the MgNd thin film. It is found that the MgNd thin film has a low work function of 3.5 eV, leading to its application in hybrid poly(3,4-ethylenedioxythiophene)-poly(styrene sulfonate) (PEDOT:PSS)/n-Si solar cells as a back surface field (BSF) material. By introducing a MgNd thin film into the back Si/electrode interface of a hybrid solar cell, obvious improvements in the open circuit voltage (V_{oc}) and fill factor (FF) of the device are observed, leading to an increase by more than 26% in power conversion efficiency (PCE). Temperature-dependent current density–voltage (J - V) and V_{oc} -light intensity measurements demonstrate that the introduction of a MgNd thin layer increases the built-in voltage at the rear interface and decreases the recombination current in the device. These improvements are attributed to the efficacy of the MgNd thin film as a BSF by reducing minority carrier recombination and enhancing majority carrier transport.

1. Introduction

In addition to p-n junctions, the formation of a back surface field (BSF) on the rear side of the Si wafer is also important in crystalline silicon (c-Si) solar cells Li et al., 2016; Plekhanov et al., 2001; Hayakawa et al., 2012. BSF favours majority carrier transport and suppresses minority carrier recombination (Yang, 1982; Rattanapan et al., 2011). From the energy band theory, in n-type c-Si solar cells, BSF can be understood as constructing a downward energy band at the rear surface of the cell to provide a field with the same direction as the built-in field in the front p-n junction (Bullock et al., 2016; Rahmouni et al., 2010).

Alternatively, organic-inorganic hybrid solar cells based on c-Si and a conductive polymer, poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS), have garnered much research interest because of their simple fabrication and potentially low-cost process (Liu et al., 2015; Wei et al., 2013; Liu et al., 2017). The PEDOT:PSS/Si heterojunction at the front side of the device is a hybrid Schottky junction, which is the focus of the vast majority of publications in this field for the study of the organic emitter properties (McGillivray et al., 2016; Jackle et al., 2015; Wang et al., 2011), hybrid interface

modification (Sheng et al., 2014; Nam et al., 2017; Zhang et al., 2017; Chi et al., 2014), Si bulk doping (Pietsch et al., 2014) and stability improvement (Hossain et al., 2016; He et al., 2014). However, similar to other c-Si solar cells, BSF is equally important for improving the performance of hybrid solar cells. Experimentally, a conventional BSF can be formed by the addition of a dopant, such as phosphorus and boron, into the Si bulk or deposited Si thin films under high temperature (Singha and Solanki, 2017; Goyal et al., 2016; Ryu et al., 2016). This method is not only energy-consuming but also creates additional impurity defects. A potential progressive scheme uses a dopant-free back contact by introducing low work function (ϕ) materials, such as LiF, Cs₂O and even the organic semiconductor 8-hydroxyquinolinolathium (LiQ), between c-Si and the back electrode (Zhang et al., 2014; Zhang et al., 2015; Zhang et al., 2014). To date, except for these materials, there has been little investigation into the BSF of hybrid solar cells.

This study offers a concept of an intermetallic BSF, by the introduction of a low- ϕ MgNd intermetallic thin film between the rear surface of the c-Si substrate and the electrode to achieve a downward energy band, for improving the photovoltaic (PV) performance of hybrid solar cells. MgNd alloy has been previously investigated as a

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structural material in the automotive and aerospace fields due to its advantageous properties such as lightweight, high strength and good castability (Wang et al., 2007; Thomas and Leung, 2014). In this work, we find that its thin film possesses a ϕ of 3.5 eV, less than the electron affinity for n-Si (4.0 eV), which inspires us to investigate its application in organic-inorganic hybrid solar cells.

2. Experimental

The wafers used in this work were those typically used in the Si PV industry, i.e., double-side-pyramidal-textured, n-type CZ wafers with a thickness of 180 μm and resistivity of $\sim 2 \Omega\text{-cm}$. The samples were first cleaned by a solution of $\text{HCl}:\text{H}_2\text{O}_2:\text{H}_2\text{O}$ (1:1:8) at 80 $^\circ\text{C}$ for 10 min followed by immersion in HF (5%) solution for 3 min. PEDOT:PSS (Clevis PH1000) with 6 wt% ethylene was spin coated on the cleaned c-Si at 3500 rpm and then annealed at 130 $^\circ\text{C}$ for 10 min. The MgNd thin film was deposited from a highly pure alloy target (Mg:Nd = 90:10 wt%) on the other side of the wafer at room temperature by an RF magnetron sputtering at a power of 80 W in a 1 Pa Ar atmosphere. Subsequently, a 300-nm-thick Ag thin film was *in situ* deposited without breaking the vacuum at the same deposition parameters as those used to deposit MgNd. Note that for Ag deposition, a two-step power method was used to decrease the damage to the MgNd BSF layer by sputter-induced ion bombardment, which was performed at a low power of 10 W for 1 min and further switched to a high power of 80 W for 5 min. The sample with only a back Ag electrode was processed individually for the fabrication of the Ag thin film. The $\sim 3 \times 3 \text{ cm}^2$ samples were cut into $\sim 1.5 \times 1.5 \text{ cm}^2$ pieces before the Ag metal grid was thermally evaporated onto the front side of the samples using a shadow mask. Finally, the $\sim 1.5 \times 1.5 \text{ cm}^2$ cells with the top electrode were cut into $1 \times 1 \text{ cm}^2$ solar cells to remove the conductive metal thin film at the edge deposited during sputtering and/or thermal evaporation. The work function of the MgNd thin film was measured on a Thermo Scientific ESCALab 250Xi (He I, 21.22 eV) by ultraviolet photoelectron spectroscopy (UPS), which was recorded with a sample bias of -10 V , and an Au standard sample was used for the Fermi level (E_{Fermi}) and binding energy calibrations. The microstructure and surface morphology of the MgNd thin films were identified by X-ray diffraction (XRD) (Bruker D8 Advance) and atomic force microscopy (AFM) (Bruker Multimode 8). The PV performances of the solar cells were characterized by their current density-voltage (J - V) plots under standard test conditions (AM1.5, 100 mW/cm^2 and 25 $^\circ\text{C}$) and suns- V_{oc} plots using a Sinton tool (WCT-120). The optical properties of the samples were characterized using a UV-Vis-NIR spectrophotometer (Hitachi U4100).

3. Results and discussion

Fig. 1(a) shows the He I UPS spectrum of the MgNd film. Its inelastic electron cutoff (E_{cutoff}) and E_{Fermi} of the corresponding Au calibration were obtained. From these data, the ϕ of MgNd was determined to be 3.5 eV (Eq. (1)) Liao et al., 2000.

$$\phi = h\nu - (E_{\text{Fermi}} - E_{\text{cutoff}}) \quad (1)$$

Such a low ϕ is beneficial to form a downward energy band at the MgNd/n-Si metal-semiconductor contact (Fig. 1(b)) to achieve a BSF function similar to the diffused n-n⁺ high-low junction (Fig. 1(c)) in traditional c-Si solar cells, i.e., favouring majority carrier transport and suppressing minority carrier recombination. However, at the contact between a high ϕ metal electrode (e. g. Ag) and Si, upward band bending is always obtained (Fig. 1(d)), which impedes majority carrier transport and increases interface recombination.

Fig. 2 shows the microstructure and surface morphology of the MgNd thin film. The MgNd thin film is well crystallized with a random crystallographic orientation (Fig. 2(a)) and smooth surface with uniform grain distribution and a small root-mean-square (RMS) roughness of 3.1 nm (Fig. 2(b)). It is found that the surface morphology of MgNd

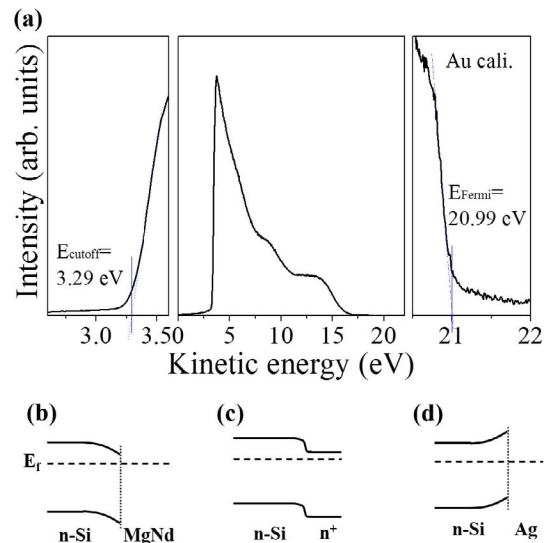


Fig. 1. (a) He I UPS spectrum of the MgNd film and the corresponding Au calibration (cali.). Band diagrams of (b) n-Si/MgNd, (c) n-Si with a heavy doping region (n-n⁺) and (d) n-Si/Ag.

film morphology is the dependence of the thickness (d) (Fig. 2(b) vs Fig. 2(c)), but the deposition rate (R_D) has no obvious effect on MgNd morphology (Fig. 2(c) vs Fig. 2(d)). A MgNd thin film was also deposited on a glass substrate to measure its conductivity using a pair of Ag coplanar gap-cell electrodes. It was found that the conductivity of MgNd is $\sim 110 \text{ n}\Omega\text{-cm}$, suggesting relatively good electrical properties.

MgNd thin layers with thicknesses ranging from 10 to 150 nm were inserted between the Si substrate and back electrode to examine its application in hybrid solar cells. The PV performance parameters of the devices are plotted in Fig. 3. The devices without the MgNd BSF had open circuit voltages (V_{oc}) of $\sim 472 \text{ mV}$ and fill factors (FF) of $\sim 63\%$. However, for the devices with the MgNd BSF, the V_{oc} and FF increased to 545 mV and 71%, corresponding to power conversion efficiency (PCE) increases from 8.7% to 11.0% (the PCE of the champion cell reaches 11.2%). This improvement in V_{oc} and FF are attributed to the change in the rear interface energy band structure, i.e., from upward (Fig. 1(d)) to downward (Fig. 1(b)) bending, which reduces minority carrier recombination and favours majority carrier transport. The PV performances of the hybrid devices with the MgNd BSF layer are hardly dependent on the thickness of the MgNd layer, possibly because of the good conductivity of the MgNd thin films. Compared with the cells containing only the Ag electrode, the short circuit current (J_{sc}) of the devices with the MgNd thin layer slightly decreased. EQE measurements were employed to explore the J_{sc} loss. As shown in Fig. 4(a), a slight QE loss was observed at the long wavelength region. Fig. 4(b) presents the reflectance measurements of the $\text{SiN}_x/\text{n-Si}/\text{Ag}$ and $\text{SiN}_x/\text{n-Si}/\text{MgNd}/\text{Ag}$ samples, in which SiN_x was selected to ensure enough incident light inside the Si bulk due to its excellent anti-reflection effect. The difference in reflectance between the two samples is attributed to the different internal reflections at the Si/Ag and Si/MgNd interfaces. Clearly, the MgNd thin film has a relatively low infrared light reflection compared to the Ag thin film, which is attributed to its higher infrared light absorption (Fig. 4(c)).

The effect of the MgNd BSF layer on the carrier transport in the device is reflected by the J - V characteristics of the solar cells without and with the MgNd layer at different test temperatures, as shown in Fig. 5(a) and (b), respectively. With an increase in the test temperature, the device with the MgNd BSF layer shows a more obvious temperature response. For example, when the test temperature of the sample increased from 130 $^\circ\text{C}$ to 140 $^\circ\text{C}$, J at -1 V clearly increased for the device with MgNd but showed only a slight variation for that without MgNd. This temperature-sensitivity is linked to thermal-induced electron

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