High-Quality ITO/Al-ZnO/n-Si Heterostructures with Junction Engineering for Improved Photovoltaic Performance

Chong Tong 1, Manjeet Kumar 2, Ju-Hyung Yun 2,*, Joondong Kim 2,*, and Sung Jin Kim 3,4*

1 Department of Electrical Engineering, State University of New York at Buffalo, Buffalo, NY 14260, USA; chongton@buffalo.edu
2 Department of Electrical Engineering, Incheon National University, Incheon 406772, Korea; manuhp1@gmail.com
3 Department of Electrical and Computer Engineering, University of Miami, Coral Gables, FL 33146, USA; kim@miami.edu
4 Biomedical Nanotechnology Institute (BioNIUM), University of Miami, Miami, FL 33142, USA
* Correspondence: juhyungyun@inu.ac.kr (J.-H.Y.); joonkim@inu.ac.kr (J.K.); Tel.: +82-32-835-8435 (J.-H.Y.); +82-32-835-8770 (J.K.); Fax: +82-32-835-0773 (J.-H.Y. & J.K.)

Abstract: A heterostructure of Sn-doped In$_2$O$_3$ (ITO)/Al-doped ZnO (AZO)/n-Si was proposed and studied for photovoltaics. The top ITO worked as a transparent conducting layer for excellent optical transparency and current collection. The AZO/n-Si served as the active junction and provided the built-in potential ($qV_{bi}$) for the photovoltaic devices. To achieve a higher open circuit voltage ($V_{oc}$), which is the main challenge for AZO/Si heterojunctions due to the junction interfacial defects, the AZO and AZO/Si junction properties were systematically investigated. By modulating the Al doping in the AZO thin films via a dual beam co-sputtering technique, the AZO/n-Si junction quality was significantly improved with $qV_{bi}$ increased from 0.21 eV to 0.74 eV. As a result, the $V_{oc}$ of our best device was enhanced from 0.14 V to 0.42 V, with a short circuit current ($J_{sc}$) of 26.04 mA/cm$^2$ and a conversion efficiency ($E_{ff}$) of 5.03%. To our best knowledge, this is the highest $V_{oc}$ reported for ZnO/Si heterojunctions prepared by the sputtering method. The results confirmed the validity of our proposed structure and junction engineering approach and provided new insights and opportunities for ZnO/Si heterojunction optoelectronics.

Keywords: Al-ZnO/Si heterojunction photovoltaic; junction engineering; built-in potential; thin film stress release

1. Introduction

ZnO, a transparent conducting oxide (TCO) material with a wide direct bandgap and a high exciton binding energy has been widely studied for various optoelectronic applications such as light emitting diodes (LEDs), laser diodes, photodetectors, and photovoltaics [1-9]. Typically, group III (B, Al, Ga, In) elements in the periodic table are employed as dopants in ZnO. Undoped ZnO has an electron affinity of 4.35 eV and direct bandgap energy of 3.28 eV with ~ 10$^{17}$ cm$^{-3}$ of an electron concentration. However, transparent heavily Al-doped and Ga-doped ZnO have been demonstrated to have low resistivity with $10^2$ ~ $10^3$ cm$^{-3}$ of electron concentration. Very low resistivities of Al-doped ZnO (AZO) and Ga doped ZnO (GZO) were reported to be ~ 8.5 x 10$^{-5}$ Ω-cm and ~ 8.1 x 10$^{-5}$ Ω-cm, respectively, which are comparable with ~ 7.7 x 10$^{-5}$ Ω-cm of resistivity of In$_2$O$_3$ (ITO) [10]. Moreover, higher transparency, better thermal stability, and low growth temperature make AZO and GZO much more promising [11,12]. ZnO-based TCOs have a relatively large refractive index in the range of
2.1 ~ 1.9 at the visible light spectra. This optical property can improve internal light absorption in conventional semiconductor materials.

In recent researches, Al-doped ZnO (AZO)/Si heterostructures demonstrated reliable rectifying junction behaviors with improved optical absorption and current collection for enhanced photovoltaic performance [13,14]. The TCO/Si device structure could provide opportunities to overcome some challenges of conventional solar cell structures, such as the lateral component of photogenerated current reduction due to emitter layer Ohmic loss. Although such a loss could be compensated for by using a heavily doped emitter layer, it could still cause higher carrier recombination with decreased light absorption. These limitations could be addressed by using well-designed TCO/Si heterojunction device structures, attributed to the superior optical transparency and electrical conductivity of TCO materials. In addition, the device fabrication process could also be simplified compared to conventional solar cells [15]. However, a main challenge of TCO/Si devices is the relatively low open circuit voltage (Voc) and fill factor (FF) performance due to the intrinsic defects and lattice mismatch at the heterojunction interfaces [11]. Thus, improving junction interfacial qualities with higher junction built-in potential values (qVbi) is essentially important [16–18].

Several demonstrations of ZnO/Si heterojunction solar cells have been reported. Chen L. et al. utilized ZnO by MOCVD method and obtained conversion efficiency of 2.82% with Voc: 294.4 mV, Jsc: 26.108 mA/cm², and FF: 36.66%, respectively [19]. L. Shen et al. reported a 1.14% of conversion efficiency of AZO/Si solar cell using Atomic Layer Deposition [20]. Ismail R. et al. used thermal oxidation of Zn dots and recorded conversion efficiency of 6.79% with Voc: 375 mV, Jsc: 25 mA/cm², and FF: 72%, respectively [21]. Das D. et al. reported a conversion efficiency of 2.51% from Si doped ZnO with a sputtering method on Si [22]. The record high efficiency has been reported by R. Pietruszka with the efficiency of 14% (Voc: 520 mV, Jsc: 38 mA/cm², and FF: 71%) and 10% (Voc: 470 mV, Jsc: 32 mA/cm², and FF: 69%) for textured and planar structures, respectively, which jump up to theoretical efficiency of 21%. In Pietruszka’s report, the hydrothermal method and the ALD method were used to grow AZO/Zn1-xMgxO films on a Si [23].

In our previous work, a bi-layer TCO structure (ITO on AZO) was reported with an improved figure of merit for both electrical and optical properties. Moreover, ITO thin films grown on AZO showed high crystalline qualities due to the hetero-epitaxial growth mechanisms [24]. In this paper, besides these benefits, the AZO/Si heterojunction and interfacial properties were studied systematically. Enhanced heterojunction properties with improved qVbi values were achieved by junction engineering via a dual beam co-sputtering technique. The best device we obtained showed an increased Voc from 0.14V to 0.42 V, with a short circuit current (Jsc) of 26.04 mA/cm² and a conversion efficiency (Eff) of 5.03%. To our best knowledge, this is the highest Voc value reported for ZnO/Si heterostructure devices prepared by the sputtering method. Our proposed structure and the demonstrated approach provided new opportunities for ZnO/Si heterojunction optoelectronics.

2. Materials and Methods

ITO and AZO were deposited on top of an n-Si substrate to fabricate ITO/AZO/Si heterojunction devices. Firstly, AZO was deposited on chemically cleaned n-type Si substrate by a dual beam co-sputtering method. Two separated 4-inch targets of ZnO (99.999%) and Al (99.999%) were used in the same chamber. ZnO with a RF magnetron and Al with a DC magnetron were applied simultaneously for AZO co-sputtering process. A constant RF power of 300 W was used for the ZnO target. Various values of DC power (0 ~ 45 W) were applied to Al target to achieve different Al doping concentrations (0 ~ 6.89 w.t.%) in AZO thin films. Al doping concentration (wt%) in ZnO was calculated based on the material density of Al (2.7 g·cm⁻³) and ZnO (5.606 g·cm⁻³) and characterized deposited volume of Al and ZnO with controlled deposition power of Al and ZnO. The co-sputtering was performed at a substrate temperature of 300 °C with 5 mTorr working pressure in Ar gas ambient. During the deposition process, the sample was rotated (7 rpm) for uniform Al doping and thin film thickness. The deposition time was controlled to be 5 min, and the thickness of the AZO film was observed to
be ~40 nm with a SEM side view image. Then, a 250-nm-thick ITO layer was deposited on top of the AZO/Si structure without breaking the vacuum. The ITO layer was deposited with an ITO target (In$_2$O$_3$ and 10 w.t.% SnO$_2$) with 300 W DC power for 15 min in 5 mTorr Ar/O$_2$ (50/1) gas ambient at 300 °C.

For further investigation of the impact of AZO inter-layers, two different device structures (i.e., ITO/n-Si and ITO/AZO/n-Si) were prepared for comparison. For the photovoltaic devices, front and back Al contacts were deposited by thermal evaporation. The fabricated devices had a 0.5 cm by 0.5 cm active area with a front grid shadowing area of 13.9%. With the same fabrication process, 1-mm-diameter circular diodes of AZO/n-Si were also fabricated to investigate the AZO/Si heterojunction properties. The thicknesses of each layer were measured by a field emission scanning electron microscope (FESEM, FEI Sirion). Secondary ion mass spectrometer (SIMS, CAMECA IMS 7f magnetic sector) characterizations were carried out to investigate the chemical depth profile for each layer in the ITO/AZO/Si structures. The crystal structure was studied by using an X-ray diffractometer (XRD, Rigaku Ultima IV). The AZO/n-Si circular diodes were analyzed by capacitance-voltage (C-V) measurement (HP 4280A) to understand the junction characteristics. Photovoltaic properties were measured using a Keithley2400 source meter under dark and illumination conditions (100 mW/cm$^2$ of AM1.5G solar spectrum, Newport, Xenon 300W).

3. Results and Discussions

Bilayer Matrix of two TCOs (ITO and AZO) was introduced to form a heterojunction with n-Si. Each layer provides optical and electrical functionality to enhance photovoltaic performance. The ITO provides high visible transparency (75.3% averaged over 400 ~ 1100 nm of wavelength) and low resistivity. ($\rho = 1.53 \times 10^{-4}$ Ω·cm and $\mu = 42$ cm$^2$/V·s) The Al modulated AZO layer was systematically investigated regarding optical and electrical properties. In Figure 1a, the measured photoluminescence (PL) spectra show two distinguishable peaks, broad green emission (2.6 ~ 2.7 eV), and near band-edge emission (3.16 ~ 3.4 eV). The defects or impurities related to green emission signals [25] were observed, and the signal strengths varied by different Al doping concentrations. The relative strength of the green emission was strongly dependent on the crystal surfaces [26]. The ratio of Igreen emission /Inear band edge was 0.42, 0.6, 1.82, and 0.56, for 0, 3.14, 4.07, and 5.22 wt% of Al doping, respectively. The intensity was enhanced with an increase of Al doping and abruptly diminished at 5.22 wt% of Al. It indicated that increased Al doping deteriorates the crystallinity of ZnO. However, when Al doping reached the proper amount—5.22 wt%—crystallinity was recovered with suppressed defects. This can be explained by released residual compressive stress by substituting the Zn sites with Al atom, and it resulted in improved crystallinity of ZnO14 [27]. The increase of Al doping shifted the peak of near band-edge emission from 3.16 eV (Al 0 wt%) to 3.4 eV (Al 5.22 wt%) due to Burstein–Moss shift for heavy Al doping regime [28–32].
The optical transmittance spectra of ZnO with different Al doping was shown in Figure 1b. The optical absorption coefficient (α) was calculated using Equation (1), where \(d\) is a ZnO thickness and \(T\) is an optical transmittance.

\[
\alpha = \frac{1}{d} \ln \left( \frac{1}{T} \right) \tag{1}
\]

The optical band gap of ZnO was extracted by linear interpolation of \((\alpha h \nu)^2\) versus \(h \nu\), based on the \(\alpha\) given in Equation (1), since ZnO is direct bandgap material and it satisfies Equation (2) [33].

\[
(\alpha h \nu)^2 = A(h \nu - E_g) \tag{2}
\]

where \(h \nu\) is photon energy, \(E_g\) is the bandgap of ZnO, and \(A\) is a constant that arises from Fermi’s golden rule for fundamental band-to-band electronic transitions.

Over the visible range, optical transmittances of all AZO films were higher than 85%. The optical band gap (\(E_g\)) measured by absorption spectra was higher than \(E_g\) achieved from near band-edge by PL, with both presenting abrupt \(E_g\) widening beyond 4.65 wt% of Al. In Figure 1c, \(E_g\) achieved by emission spectra was gradually reduced when Al doping was higher than 5.78 wt%. This phenomenon was reported to have involved many-body effects [28–30]. The energy difference (\(\Delta E_g\)) of \(E_g\) measured by photoemission (by PL spectra) and photoabsorption (by transmittance spectra) clearly shows Stokes shift (0.06 eV at Al 0 wt% ~ 0.24 eV at Al 6.34 wt%). In Figure 1c, above 5.78 wt% of Al, stoke shift was drastically increased, which can be explained by the fact that excessive Zn interstitials induced inhomogeneous strain inside AZO [34,35]. Electrical properties were characterized by Hall effect.
measurement, as shown in Figure 1d. AZO films have n-type polarity. Carrier concentration was increased from $5 \times 10^{16}$ cm$^{-3}$ (Al 0 wt%) to $4.5 \times 10^{20}$ cm$^{-3}$ (Al 6.34 wt%) by adding Al in AZO. Highest electron mobility, 15 cm$^2$/V·s, was achieved at Al 5.78 wt%. The excessive Al doping with 6.89 wt% fully deteriorates crystal quality, as shown in quenched PL near band edge peak (Figure 1a), large Stoke shift (Figure 1c), and decreased electron mobility (Figure 1d).

The proposed ITO/AZO/n-Si device structure and the cross-section scanning electron microscope (SEM) image were shown in Figure 2a,b, respectively. Bilayer TCO structure (ITO and AZO) was introduced to enhance both the optical and electrical performance of the photovoltaic devices [36]. In ITO/AZO/n-Si devices, the top ITO layer worked as a transparent conducting layer, providing high optical transparency and superior current collection efficiency. The device current transport mechanism was mainly determined by using the AZO/Si heterojunction, which provided the active junction built-in potential ($qV_{bi}$) for the photogenerated carrier separation under the illumination [37,38]. The theoretical AZO/n-Si junction band diagram before and after equilibrium conditions are shown in Figure 2c [36,37].

![Figure 2](image_url)

**Figure 2.** (a) Schematics of the In$_2$O$_3$ (ITO)/ Al-doped ZnO (AZO)/Si heterostructure solar cell devices, (b) cross-sectional SEM image of the ITO/AZO/Si structure, and (c) theoretical energy band alignment of AZO/n-Si heterojunction before and after equilibrium condition.

To better understand the ITO/AZO/Si structure properties, the chemical composition depth profiles of ITO/AZO/Si structures were characterized via a secondary ion mass spectrometer (SIMS). The AZO inter-layers with different Al doping concentrations were deposited via the dual-beam co-sputtering method (details in the Experimental Section). As shown in Figure 3a–c, they were prepared with the same ZnO sputtering power of 300 W, but different Al co-sputtering powers of 15, 25, and 35 W, respectively. One can see that the element distributions of In, O, and Zn were identical across samples, indicating a stable and uniform deposition condition. Due to the different Al co-sputtering powers, different signal intensities were observed, indicating different Al doping concentrations in AZO inter-layers. This demonstrated the flexible Al doping tunability in AZO thin films via the proposed dual-beam co-sputtering method. Based on the deposition rate, the Al doping in AZO inter-layers was calculated to be 4.07, 5.22, and 6.34 w.t.%, as shown in Figure 3a–c, respectively.
Figure 2. Schematics of the In$_2$O$_3$ (ITO)/Al-doped ZnO (AZO)/Si heterostructures with 4.07 wt%, 5.22 wt %, and 6.34 wt% of Al doping in the AZO inter-layers, respectively. ITO (~250 nm) was grown by a DC magnetron sputtering. AZO (~40 nm) layer was grown by the dual-beam co-sputtering method.

Figure 3. Secondary ion mass spectrometry (SIMS) analysis of ITO/AZO/n-Si structures. (a)–(c) showed the depth profiles of indium (In), oxide (O), zinc (Zn), aluminum (Al), and silicon (Si) in ITO/AZO/n-Si heterostructures with 4.07 wt%, 5.22 wt %, and 6.34 wt% of Al doping in the AZO inter-layers, respectively. ITO (~250 nm) was grown by a DC magnetron sputtering. AZO (~40 nm) layer was grown by the dual-beam co-sputtering method.

The level of Al doping in AZO thin films affects the AZO/n-Si heterojunction and interface properties. They are essentially important for AZO/Si heterojunction photovoltaic device performance. Proper junction and interface engineering can benefit the heterojunction built-in potential ($qV_{bi}$) and the device carrier transport mechanisms, providing enhanced $V_{oc}$ and FF performance. However, the actual energy band alignment between AZO and Si heterojunction can be complicated. The AZO doping concentration can affect not only the Fermi energy level ($E_F$), but also other parameters such as electron affinity ($\chi$) [39]. The band alignment is also affected by the AZO thin film properties, such as the electrical conductivity, oxygen deficiency, and the deposition conditions [39,40]. In this work, the $qV_{bi}$ values of AZO/n-Si heterojunctions were extracted via capacitance-voltage (C-V) measurement. The capacitance of the AZO/Si heterojunction can be described as below:

$$\frac{1}{C^2} = \frac{2}{qA^2} \varepsilon_0 \varepsilon_{AZO} N_{AZO} + \varepsilon_{Si} N_{Si} (V_{bi} - V)$$

where $\varepsilon_0$: free space permittivity, $\varepsilon_{AZO}$, and $\varepsilon_{Si}$: relative dielectric constants of AZO and Si, $N_{AZO}$ and $N_{Si}$: doping concentrations of AZO and Si, $V_{bi}$: build-in voltage, $V$: bias voltage, and $A$: device area.

Since the doping level of AZO is much higher than that of Si (i.e., $N_{AZO} \gg N_{Si}$), Equation (3) can be rewritten as

$$\frac{1}{C^2} = \frac{2}{A^2 q \varepsilon_0 \varepsilon_{Si} N_{Si}} (V_{bi} - V)$$

Using Equation (4), the $qV_{bi}$ values were extracted via the linear fitting of $\frac{1}{C^2}$ vs. $V$. As shown in Table 1, one can see that moderately increasing Al doping concentration in AZO thin films from 4.65 w.t.% to 6.34 w.t.% could significantly improve AZO/n-Si $qV_{bi}$ values from 0.21 eV to 0.74 eV. The higher $qV_{bi}$ value could benefit the photogenerated carrier separation and suppress recombination at the junction interface, providing better current transport efficiency with higher $V_{oc}$ and FF performance [41].

| Al Doping in AZO (w.t.%) | Built-in Potential ($qV_{bi}$) of AZO/n-Si Junction |
|--------------------------|-----------------------------------------------------|
| 4.65 w.t.%               | 0.21 eV                                              |
| 5.78 w.t.%               | 0.46 eV                                              |
| 6.34 w.t.%               | 0.74 eV                                              |
In order to understand the increased $qV_{bi}$ values and the related junction interface characteristics, the AZO crystallinity and the thin film residual stress were systematically investigated. In this work, the AZO thickness was relatively thin (40 nm), thus the residual stress is a significant factor of AZO thin film properties as reported [42]. As shown in Figure 4a, the AZO thin films with various Al doping concentrations (i.e., 4.65 wt%, 5.22 wt %, and 6.34 wt%) all showed XRD diffraction peak positions of $2\theta$ around $\sim$34.4°, indicating a preferential crystalline orientation of (002) with the c axis perpendicular to the substrates. For the AZO with Al doping of 4.65 wt% (as shown in the upper panel of Figure 4a), the XRD peak was at $2\theta$ of 34.39°, which is slightly lower than the pure (002) ZnO powder value (i.e., $2\theta = 34.47°$). This slight deviation indicated a tensile residual stress parallel to the c axis caused by the imperfection of the AZO crystal structure and the atom impacting effects during the sputtering process. For AZO with slightly higher Al doping concentrations of 5.22 wt.% and 6.34 wt.% (as shown in the middle and bottom panels of Figure 4a), the peak position shifted to larger $2\theta$ angles of 34.43° and 34.49°, respectively. This shift implied that the spacing between AZO (002) planes was shortened, and the tensile stress was reduced with the increase of Al doping. The ionic radius of Al$^{3+}$ (~53 pm) is smaller than that of Zn$^{2+}$ (~72 pm). When moderate Al doping atoms were introduced into AZO thin films substituting the Zn sites, the length between (002) planes was reduced with tensile stress released². The actual residual stress ($\sigma$) of the AZO thin films can be calculated via Equations (5) and (6) as below [43]:

$$\sigma = \frac{2c_0^2 - c_0c_{13}(c_{11} + c_{13})}{2c_{13}c_0} \frac{c - c_0}{c_0}$$  \hspace{1cm} (5)
$$2d \sin \theta = \lambda$$  \hspace{1cm} (6)

where, the elastic constants of ZnO single crystal are $c_{11} = 208.8$ GPa, $c_{33} = 213.8$ GPa, $c_{12} = 119.7$ GPa, and $c_{13} = 104.2$ GPa; $c_{12} = 0.5201$ nm is the stress-free ZnO lattice constant. $d$ is the space between (002) planes of the AZO thin films; $c = 2d$ is the lattice constant for AZO thin films. $\lambda$ is the X-ray wavelength (1.5418 Å), and $\theta$ is the Bragg diffraction angle.

![Figure 4](image-url)

Figure 4. (a) X-ray diffraction patterns of AZO (002) with different Al doping concentrations and (b) AZO thin film grain size, residual strain, and $qV_{bi}$ of AZO/n-Si junctions with different Al doping concentrations.

As shown in Figure 4b, the calculated tensile stress ($\sigma$) values decreased from $6.74 \times 10^8$ Pa to $4.0 \times 10^8$ Pa and $0.08 \times 10^8$ Pa for the AZO thin films with Al doping of 4.65 wt%, 5.22 wt.%, and 6.34 wt.% respectively.
Additionally, the average crystal grain sizes \((D)\) for the AZO thin films were also extracted by using Equation (7) as follows:

\[
D = \frac{K\lambda}{\beta \cos \theta}
\]

where \(\lambda\) is the X-ray wavelength, \(\beta\) is the full width at half-maximum (FWHM) of the (002) diffraction peak, \(\theta\) is the Bragg diffraction angle, and \(K\) is a constant of 0.94.

The average grain size for the AZO with Al dopings of 4.65 w.t.%, 5.22 w.t.% and 6.34 w.t.% was 12.4 nm, 17.3 nm, and 34.2 nm, respectively. As shown in Figure 4b, the extracted AZO thin film structural parameters (i.e., residual stress and grain size) were compared with the AZO/Si heterojunction \(qV_{bi}\) values for difference Al doping in AZO. One can see that by moderately increasing Al doping in AZO films from 4.65 w.t.% to 6.34 w.t.%, the thin film residual stress reduced dramatically from \(6.74 \times 10^8\) Pa to \(0.08 \times 10^8\) Pa. As a result, the crystal grain size increased from 12.4 nm to 34.2 nm, due to the low surface free energy and enhanced ZnO thin film crystallinity provided by the residual stress release [44]. The built-in potential \((qV_{bi})\) of AZO/Si junction was also improved from 0.21 eV to 0.74 eV, indicating the heterojunction and interface quality enhancement. As previously reported, due to relatively large lattice and thermal expansion mismatch between AZO and Si, AZO thin films deposited on Si were expected to have high residual stress and heterojunction interfacial defects [45–47]. In this work, junction engineering was performed by adding moderate Al doping into AZO thin films via the dual-beam co-sputtering technique. The AZO thin film residual stress was significantly released with enhanced AZO crystallinity and junction built-in potential. This approach benefits our proposed ITO/AZO/Si heterojunction photovoltaic structures.

Finally, the fabricated ITO/AZO/n-Si solar cell device was characterized to determine the photovoltaic performance. The ITO/n-Si devices without AZO inter-layers were also fabricated for comparison. As shown in Figure 5a, the ITO/n-Si device provided a \(J_{sc}\) value of 16 mA/cm² with a relatively low \(V_{oc}\) and FF performance of only 0.14 V and 0.28, respectively. By introducing AZO inter-layers with moderate Al doping for junction engineering, a significant improvement could be achieved, as shown in Figure 5b. The \(V_{oc}\) and FF showed improvement from 0.14 V to 0.42 V and from 0.24 to 0.46, respectively. This improved device performance confirms that the AZO film with a delicately controlled Al doping can improve the AZO crystallinity and the thin film stress release, resulting in better AZO/Si heterojunction characteristics.

Moreover, the photocurrent \((J_{sc})\) enhancement was observed with increasing Al doping in AZO. This can be explained by the AZO band gap widening effect, as described by the Burstein–Moss shift [48]. As shown in Figure 5c, the photovoltaic device performance characteristics were extracted for ITO/AZO/n-Si devices with different Al doping concentrations. The photovoltaic performance improved with moderately increasing Al doping concentrations from 0 w.t.% to ~6.34 w.t.% in AZO inter-layers. The best performance device (i.e., Al doping in AZO of 6.34 w.t.%) achieved the overall conversion efficiency (Eff) of 5.03%, with \(J_{sc}\) and \(V_{oc}\) of 26.04 mA/cm² and 0.42 V, respectively. To the best of our knowledge, this is the highest \(V_{oc}\) value reported for ZnO/Si heterojunction devices prepared by the sputtering method. One can also see in Figure 5c that when the Al doping concentration was too high (i.e., ~6.89 w.t.%), the device performance rapidly decreased due to the deteriorated AZO thin film and junction properties. The overall performance enhancement of our best cell confirmed the validity of our proposed device architecture and the junction engineering approach. The performance could be further improved by optimizing light absorption via antireflection coating and nanoplasmonic structures [49–51].
Figure 5. Photo I-V characteristics of (a) ITO/n-Si and (b) ITO/AZO/n-Si heterostructure devices with different Al dopings in AZO inter-layers (under AM1.5G illumination). (c) Photovoltaic characteristics extracted for ITO/AZO/n-Si devices with different Al doping in AZO.

4. Conclusions

ITO/AZO/n-Si heterostructure was proposed for enhanced photovoltaic applications. The ITO thin film on the top served as a transparent conducting window layer. The AZO inter-layer was deposited on an n-Si substrate to form a high-quality AZO/Si heterojunction via a dual-beam co-sputtering technique. It allowed junction engineering by introducing uniform Al doping in AZO with precise control of the doping concentrations. With moderate Al doping (i.e., Al: 6.34 w.t.%), the thin film residual stress was significantly released from 6.74 × 10^8 Pa to 0.08 × 10^8 Pa, which improved the AZO crystalline characteristics and the AZO/Si junction qualities. This boosted the qV_{bi} of AZO/n-Si heterojunction from 0.21 eV to 0.74 eV and provided enhanced V_{oc} photovoltaic performance from 0.14 V to 0.42 V. The best device we obtained showed a conversion efficiency (Eff) of 5.03% with J_{sc} of 26.04 mA/cm^2 and V_{oc} of 0.42 V. To the best of our knowledge, this is the highest V_{oc} value reported for ZnO/Si heterojunction devices prepared by a sputtering method. The results demonstrated the validity of our proposed structure and junction engineering approach, which could provide new insights and opportunities for ZnO/Si heterojunction photovoltaics.

Author Contributions: Supervision, J.-H.Y. and J.K.; Writing—original draft, C.T.; Writing—review and editing, M.K., S.J.K., J.-H.Y., and J.K. All authors have read and agreed to the published version of the manuscript.

Funding: The authors acknowledge the financial support of Incheon National University Research Grant in 2018.

Conflicts of Interest: The authors declare no conflict of interest.

References
1. Pietruszka, R.; Schifano, R.; Krajewski, T.A.; Witkowski, B.S.; Kopalko, K.; Wachnicki, L.; Zielony, E.; Gwozdz, K.; Bieganski, P.; Placzek-Popko, E.; et al. Improved efficiency of n-ZnO/p-Si based photovoltaic cells by band offset engineering. Sol. Energy Mater. Sol. Cells 2016, 147, 164–170. [CrossRef]
2. Tong, C.; Yun, J.; Chen, Y.; Ji, D.; Gan, Q.; Anderson, W.A. Thermally diffused al: ZnO thin films for broadband transparent conductor. ACS Appl. Mater. Interfaces 2016, 8, 3985–3991. [CrossRef] [PubMed]

3. Cheng, C.W.; Sie, E.J.; Liu, B.; Huan, C.H.A.; Sum, T.C.; Sun, H.D.; Fan, H.J. Surface plasmon enhanced band edge luminescence of ZnO nanorods by capping Au nanoparticles. Appl. Phys. Lett. 2010, 96, 071107. [CrossRef]

4. Xiao, X.H.; Ren, F.; Zhou, X.D.; Peng, T.C.; Wu, W.; Peng, X.N.; Yu, X.F.; Jiang, C.Z. Surface plasmon-enhanced light emission using silver nanoparticles embedded in ZnO. Appl. Phys. Lett. 2010, 97, 071909. [CrossRef]

5. Haglund, R.F.; Lawrie, B.J.; Mu, R. Coupling of photoluminescent centers in ZnO to localized and propagating surface plasmons. Thin Solid Films 2010, 518, 4637–4643. [CrossRef]

6. Koleva, M.; Dikovska, A.O.; Nedyalkov, N.; Atanasov, P.; Bliznakova, I. Enhancement of ZnO photoluminescence by laser nanostructuring of Ag underlayer. Appl. Surf. Sci. 2012, 258, 9181–9185. [CrossRef]

7. Patra, A.; Das, V.D.; Kasiviswanathan, S. Optical and photoluminescence studies of gold nanoparticles embedded ZnO thin films. Thin Solid Films 2009, 518, 1399–1401. [CrossRef]

8. Xu, T.N.; Hu, L.; Jin, S.Q.; Zhang, B.P.; Cai, X.K.; Wu, H.Z.; Sui, C.H. Photon energy conversion via localized surface plasmons in ZnO/Ag/ZnO nanostructures. Appl. Surf. Sci. 2012, 258, 5886–5891. [CrossRef]

9. Patole, S.; Islam, M.; Aiyer, R.; Mahamuni, S. Optical studies of ZnO/Ag nanojunctions. J. Mater. Sci. 2006, 41, 5602–5607. [CrossRef]

10. Liu, H.Y.; Avrutin, V.; Izyumskaya, N.; Özgür, U.; Morkoc, H. Transparent conducting oxides for electrode applications in light emitting and absorbing devices. Superlattices Microstruct. 2010, 48, 458–484. [CrossRef]

11. Kaul, A.R.; Gorbenko OYu; Botev, A.N.; Burova, L.I. MOCVD of pure and Ga-doped epitaxial ZnO. Superlattices Microstruct. 2005, 38, 272–282. [CrossRef]

12. Snure, M.; Tiwar, A. Structural, electrical, and optical characterizations of epitaxial ZnO films grown on (001) GaAs substrate. J. Appl. Phys. 2007, 101, 124912. [CrossRef]

13. Yun, J.-H.; Kim, J. Double transparent conducting oxide films for photoelectric devices. Mater. Lett. 2012, 70, 4–6. [CrossRef]

14. Kim, J.; Yun, J.-H.; Park, Y.C.; Anderson, W.A. Transparent and crystalline Al-doped ZnO film-embedded heterojunction Si solar cell. Mater. Lett. 2012, 75, 99–101. [CrossRef]

15. Lee, Y.-J.; Ruby, D.S.; Peters, D.W.; McKenzie, B.B.; Hsu, J.W. ZnO nanostructures as efficient antireflection layers in solar cells. Nano Lett. 2008, 8, 1501–1505. [CrossRef] [PubMed]

16. Nakatsuka, S.; Nose, Y.; Shirai, Y. Band offset at the heterojunction interfaces of CdS/ZnSnP2, ZnS/ZnSnP2, and InS3/ZnSnP2. J. Appl. Phys. 2016, 119, 193107. [CrossRef]

17. Teran, A.S.; Chen, C.; López, E.; Linares, P.G.; Artacho, I.; Martí, A.; Luque, A.; Phillips, J.D. Heterojunction band offset limits on open-circuit voltage in p-ZnT e−xGa2xO films grown on sapphire (0001) substrate. IEEE J. Photovolt. 2015, 5, 874–877. [CrossRef]

18. Gassenbauer, Y.; Klein, A. Electronic and chemical properties of tin-doped indium oxide (ITO) surfaces and ITO/ZnO interfaces studied in-situ by photoelectron spectroscopy. J. Phys. Chem. B 2006, 110, 4793–4801. [CrossRef]

19. Chen, L.; Chen, X.; Liu, Y.; Zhao, Y.; Zhang, X. Research on ZnO/Si heterojunction solar cells. J. Semicond. 2017, 38, 054005. [CrossRef]

20. Shen, L.; Ma, Z.Q.; Shen, C.; Li, F.; He, B.; Xu, F. Studies on fabrication and characterization of a ZnO/p-Si-based solar cell. Superlattices Microstruct. 2010, 48, 426–433. [CrossRef]

21. Ismail, R.; Al-Jawad, S.H.; Hussein, N. Preparation of n-ZnO/p-Si solar cells by oxidation of zinc nanoparticles: Effect of oxidation temperature on the photovoltaic properties. Appl. Phys. A 2014, 117, 1977–1984. [CrossRef]

22. Das, D.; Karmakar, L. Optimization of Si doping in ZnO thin films and fabrication of n-ZnO/p-Si heterojunction solar cells. J. Alloy. Compd. 2020, 824, 153902. [CrossRef]

23. Pietruszka, R.; Wittkowski, B.S.; Zielony, E.; Gwozdz, K.; Placzek-Popko, E.; Godlewski, M. ZnO/Si heterojunction solar cell fabricated by atomic layer deposition and hydrothermal methods. Sol. Energy 2017, 155, 1282–1288. [CrossRef]

24. Yun, J.-H.; Kim, J.; Park, Y.C.; Moon, S.-J.; Anderson, W.A. Double transparent conducting layers for Si photovoltaics. Thin Solid Films 2013, 547, 17–21. [CrossRef]

25. Özgür, Ü.; Alivov, Y.I.; Liu, C.; Teke, A.; Reshchikov, M.A.; Doğan, S.; Avrutin, V.; Cho, S.-J.; Morkoç, H. A comprehensive review of ZnO materials and devices. J. Appl. Phys. 2005, 98, 041301. [CrossRef]
26. Zhou, X.; Kuang, Q.; Jiang, Z.-Y.; Xie, Z.-X.; Xu, T.; Huang, R.-B.; Zheng, L.-S. The origin of green emission of ZnO microcrystallites: Surface-dependent light emission studied by cathodoluminescence. J. Phys. Chem. C 2007, 111, 12091–12093. [CrossRef]

27. Kim, J.; Yun, J.-H.; Lee, S.-W.; Park, Y.C.; Ju, M.; Han, S.; Kim, Y.; Kim, J.-H.; Anderson, W.A.; Lee, J.-H.; et al. Rapid thermal annealed al-doped ZnO film for a UV detector. Mater. Lett. 2011, 65, 786–789. [CrossRef]

28. Banerjee, P.; Lee, W.-J.; Bae, K.-R.; Lee, S.B.; Rubloff, G.W. Structural, electrical, and optical properties of atomic layer deposition al-doped ZnO films. J. Appl. Phys. 2010, 108, 043504. [CrossRef]

29. Kim, K.H.; Park, K.C.; Ma, D.Y. Structural, electrical and optical properties of aluminum doped zinc oxide films prepared by radio frequency magnetron sputtering. J. Appl. Phys. 1997, 81, 7764–7772. [CrossRef]

30. Lu, J.G.; Ye, Z.Z.; Zeng, Y.J.; Zhu, L.P.; Wang, L.; Yuan, J.; Zhao, B.H.; Liang, Q.L. Structural, optical, and electrical properties of (Zn,Al)O films over a wide range of compositions. J. Appl. Phys. 2006, 100, 073714. [CrossRef]

31. Lu, J.G.; Fujita, S. Carrier concentration dependence of band gap shift in N-type ZnO: Al Films. J. Appl. Phys. 2007, 101, 083705. [CrossRef]

32. Yogamalar, N.R.; Chandra Bose, A. Burstein-moss shift and room temperature near-band-edge luminescence in lithium-doped zinc oxide. Appl. Phys. A 2011, 103, 33–42. [CrossRef]

33. Tang, G.; Liu, H.; Zhang, W. The variation of optical band gap for ZnO: In films prepared by sol-gel technique. Adv. Mater. Sci. Eng. 2013, 2013, 4. [CrossRef]

34. Das, A.K.; Misra, P.; Kukreja, L.M. Effect of s i doping on electrical and optical properties of ZnO thin films grown by sequential pulsed laser deposition. J. Phys. D Appl. Phys. 2009, 42, 165405. [CrossRef]

35. Özgür, Ü.; Teke, A.; Liu, C.; Cho, S.-J.; Morkoç, H.; Everitt, H.O. Stimulated emission and time-resolved photoluminescence in RF-sputtered ZnO thin films. Appl. Phys. Lett. 2004, 84, 3223–3225. [CrossRef]

36. Chen, Y.C.; Tong, C.; Yun, J.; Wayne, A.A. Current transport in Al-diiffused ZnO/Si heterostructures. J. Electron. Mater. 2015, 44, 96–102. [CrossRef]

37. Yun, J.; Kim, J.; Kojori, H.S.; Kim, S.J.; Tong, C.; Anderson, W.A. Current enhancement of aluminum doped ZnO-Si isotype heterojunction solar cells by embedding silver nanoparticles. J. Nanosci. Nanotechnol. 2013, 13, 5547–5551. [CrossRef] [PubMed]

38. Yun, J.; Kozarsky, E.; Kim, J.; Kojori, H.S.; Kim, S.J.; Tong, C.; Wang, J.; Anderson, W.A. Silver nanoparticles incorporated in aluminum doped ZnO for heterojunction solar cells. In Proceedings of the 38th IEEE Photovoltaic Specialists Conference (PVSC), Austin, TX, USA, 3–8 June 2012; pp. 2625–2627.

39. Klein, A.; Körber, C.; Wachau, A.; Säuberlich, F.; Gassenbauer, Y.; Harvey, S.P.; Profit, D.E.; Mason, T.O. Transparent conducting oxides for photovoltaics: Manipulation of Fermi level, work function and energy band alignment. Materials 2010, 13, 4982–4914. [CrossRef] [PubMed]

40. Min, C.-H.; Cho, S.; Lee, S.H.; Cho, D.-Y.; Park, W.G.; Chung, J.G.; Lee, E.; Lee, J.C.; Anass, B.; Lee, J.H.; et al. Effect of oxygen partial pressure on the Fermi level of ZnO-Si films fabricated by pulsed laser deposition. Appl. Phys. Lett. 2010, 96, 201907. [CrossRef]

41. Chen, A.; Zhu, K. Effects of TCO work function on the performance of TCO/Si heterojunction solar cells. Sol. Energy 2014, 107, 195–201. [CrossRef]

42. Park, S.H.; Hanada, T.; Oh, D.C.; Minegishi, T.; Goto, H.; Fujimoto, G.; Park, J.S.; Im, I.H.; Chang, J.H.; Cho, M.W.; et al. Lattice relaxation mechanism of ZnO thin films grown on c-Al2O3 substrates by plasma-assisted molecular-beam epitaxy. Appl. Phys. Lett. 2007, 91, 231904. [CrossRef]

43. Zhang, W.; Zhao, J.; Liu, Z.; Liu, Z.; Fu, Z. Influence of growth temperature of TiO2 buffer on structure and PL properties of ZnO films. Appl. Surf. Sci. 2010, 256, 4423–4425. [CrossRef]

44. Hu, S.Y.; Lee, Y.C.; Lee, J.W.; Huang, J.C.; Shen, J.L.; Water, W. The structural and optical properties of ZnO/Si thin films by RTA treatments. Appl. Surf. Sci. 2008, 254, 1578–1582. [CrossRef]

45. Wang, P.; Jin, C.; Wu, X.; Zhan, H.; Zhou, Y.; Wang, H.; Kang, J. Quality improvement of ZnO thin layers overgrown on Si(100) substrates at room temperature by nitridation pretreatment. AIP Adv. 2012, 2, 022139. [CrossRef]

46. Tong, C.; Kozarsky, E.S.; Kim, J.; Yun, J.; Anderson, W.A. Metal-induced growth of crystal Si for low-cost Al:ZnO/Si heterojunction thin film photodetectors. Mater. Sci. Semicond. Process. 2018, 82, 92–96. [CrossRef]

47. Kozarsky, E.; Yun, J.; Tong, C.; Hao, X.; Wang, J.; Anderson, W.A. Thin Film ZnO/Si Heterojunction Solar Cells: Design and Implementation. In Proceedings of the 38th IEEE Photovoltaic Specialists Conference (PVSC), Austin, TX, USA, 3–8 June 2012; pp. 1217–1219.
48. Walsh, A.; Da, S.; Juarez, L.F.; Wei, S.-H.; Körber, C.; Klein, A.; Piper, L.F.J.; DeMasi, A.; Smith, K.E.; Panaccione, G.; et al. Nature of the band gap of $\text{In}_2\text{O}_3$ revealed by first-principles calculations and X-ray spectroscopy. *Phys. Rev. Lett.* **2008**, *100*, 167402. [CrossRef] [PubMed]

49. Tong, C.; Yun, J.; Kozarsky, E.; Anderson, W.A. Nanoplasmonic Enhanced ZnO/Si heterojunction metal–semiconductor–metal photodetectors. *J. Electron. Mater.* **2013**, *42*, 889–893. [CrossRef]

50. Tong, C.; Yun, J.; Song, H.; Gan, Q.; Anderson, W.A. Plasmonic-enhanced Si Schottky barrier solar cells. *Sol. Energy Mater. Sol. Cells* **2014**, *120*, 591–595. [CrossRef]

51. Hu, H.; Zeng, X.; Tong, C.; Anderson, W.A.; Gan, Q.; Deng, J.; Jiang, S. Polarization-insensitive metal—Semiconductor—Metal nanoplasmonic structures for ultrafast ultraviolet detectors. *Plasmonics* **2013**, *8*, 239–247. [CrossRef]