Characteristics and Electronic Band Alignment of a Transparent p-CuI/n-SiZnSnO Heterojunction Diode with a High Rectification Ratio

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Abstract: Transparent p-CuI/n-SiZnSnO (SZTO) heterojunction diodes are successfully fabricated by thermal evaporation of a (111) oriented p-CuI polycrystalline film on top of an amorphous n-SZTO film grown by the RF magnetron sputtering method. A nitrogen annealing process reduces ionized impurity scattering dominantly incurred by Cu vacancy and structural defects at the grain boundaries in the CuI film to result in improved diode performance; the current rectification ratio estimated at ±2 V is enhanced from 10^6 to 10^7. Various diode parameters, including ideality factor, reverse saturation current, offset current, series resistance, and parallel resistance, are estimated based on the Shockley diode equation. An energy band diagram exhibiting the type-II band alignment is proposed to explain the diode characteristics. The present p-CuI/n-SZTO diode can be a promising building block for constructing useful optoelectronic components such as a light-emitting diode and a UV photodetector.

Keywords: copper iodide (CuI); SiZnSnO (SZTO); transparent diode; current rectification ratio; energy band alignment

1. Introduction

The γ-phase of copper iodide (CuI) with a direct bandgap (Eg) of ≈3.1 eV has been attracting increased attention as an emergent transparent p-type semiconductor with a high hole mobility (μh); for example, the μh value reaches up to ≈44 cm^2V^−1s^−1 in a single crystal, thereby being higher than that of any other conventional p-type oxides [1]. Even in a thin film form, CuI exhibits a relatively high μh of typically 6–7 cm^2V^−1s^−1 at a hole concentration (p) of ≈10^19 cm^−3 [2]. Moreover, with the additional heat treatment such as ex situ thermal annealing [3] or in situ thermal annealing during deposition [4], μh values of those films are further enhanced more up to ≈26 cm^2V^−1s^−1. Such thermal annealing processes are known to suppress not only Cu vacancy (Vc), which is the main source of acceptor in the CuI system, but also structural defects such as pinholes or grain boundaries. In this respect, the CuI thin films with proper heat treatment can play an important role of being a transparent p-type layer in various optoelectronic devices such
as solar cells [5], a light-emitting diode [6], a field-effect transistor [7], and a UV photodetector [8,9].

In order to realize a transparent p-n diode based on the CuI, we have been investigating various heterojunction diodes made of p-CuI and n-type semiconductors [2,8–11]; in our previous work, we have reported a transparent diode made of p-CuI/n-BaSnO3:Sn (BSO) films and its carrier transport behavior [12]. The realized p-CuI/n-BSO diode exhibited a high current rectification ratio \( (I_{h}/I_{o}) \) of \( 6.75 \times 10^{3} \) at an external voltage bias of \( \pm 2 \) V. On the other hand, a high-quality BSO film often requires an epitaxial growth on a proper substrate such as SrTiO3 (001), and its ideal growth temperature is rather high (\( \approx 800 \) °C). Therefore, for the applications in e.g., flexible UV photodetectors, it is desirable to test a heterojunction diode made of an alternative n-type film that can be grown at a relatively low-temperature condition comparable to that of the CuI film and without the constraint of epitaxy.

Along this line of reasoning, Yamada et al. have recently reported that a heterojunction diode made of p-CuI film and the well-known n-type amorphous semiconductor InGaZnO (IGZO) film exhibits a high rectification ratio of \( \approx 10^{6} \) [8]. Independent of this promising approach, we have been focusing on a new n-type amorphous semiconductor SiZnSnO (SZTO) film that exhibits a high optical gap \( E_{g} \) larger than 3.7 eV [13] and a field-effect mobility of \( \approx 38 \text{ cm}^{2}\text{V}^{-1}\text{s}^{-1} \) [14]. It has been found that the n-type SZTO film maintains enhanced electrical stability as compared to the IGZO film [13], which is possibly due to reduced oxygen vacancies as controlled by Si concentration via strong Si–O bonding [15]. In addition, the n-type SZTO film has another advantage of being composed of non-toxic and abundant elements of Si and Sn. Therefore, we decided to adopt the SZTO as a transparent n-type layer to realize a new heterojunction diode with the p-CuI film.

Another potential merit of the p-CuI/n-SZTO diode lies in the capability of tuning the electronic energy diagram of the n-type amorphous ZnSnO layer by the control of Si concentration. Such a capability might provide an opportunity for improving the efficiency of a potential optoelectronic device such as a light-emitting diode. As an example, Baek et al. [6] have shown that the performance of the light-emitting diode made of p-CuI/n-MgZn\(_{x}\)O quantum dot (\( x = 0, 0.7, \) and 6 at %) has improved when the energy level difference between \( n\)-MgZn\(_{x}\)O and Al electrode is adjusted via the control of \( x \). The imbalance between the injected hole and electron carriers at the interface of a light-emitting diode can potentially lead to the decreased device performance. Thus, the control of electron and hole injection ratios via a proper tuning of energy band diagram can be an effective way to improve performance of the given light-emitting diode.

Yet another promising application direction of the p-CuI/n-SZTO diode is a self-powered UV photodetector [16]. Recently, the photo-response of various p-n diode structures made of p-CuI films (or nanoparticles) and various n-type materials are widely being tested; those n-type materials include IGZO films [8], CsPbBr\(_{3}\) crystals [9], ZnO:Au films [17], and ZnO films [18], and β-GaO\(_{3}\) single crystals [19]. Once realized, those photodetectors made of the p-n diode are expected to have self-powered characteristics and reliable responsivity under UV light illumination [8,9,17,18]. Thus, the diode made of p-CuI and n-SZTO can be another promising platform for realizing a flexible, transparent UV photodetector with a capability of tuning electronic band diagram in the SZTO layer. To realize such a device, quantitative understandings on the diode performance and energy band alignment at the interface should be prerequisite.

With the above motivations, we here report the realization of transparent heterojunction diodes made of novel transparent polycrystalline p-CuI film and amorphous n-SZTO film that has resulted in a high rectification ratio \( I_{h}/I_{o} \) of \( \approx 10^{7} \). To investigate the diode characteristics, various diode parameters, such as ideality factor, reverse saturation current, and series resistance, etc., are estimated from the diode curve fitting based on the Shockley diode equation. We propose an energy band diagram of the p-CuI/n-SZTO diode exhibiting type-II heterojunction and attribute the high rectification
ratio to the improved transport properties of the Cul film, resulting from reduced ionized impurity scattering of Cu vacancies and enhanced diode interface via reduced structural defects. Our results show that the diode made of p-Cul/n-SZTO films exhibits an excellent electrical performance as a transparent pn diode with potential tunability of the energy band diagram, which can be useful for realizing flexible, cost-effective optoelectronic devices such as UV photodetectors and light-emitting diodes.

2. Experimental Section

InO:Sn (ITO, film thickness t = 50 nm) and SZTO (t = 27 nm) films were deposited on boro-aluminosilicate glass substrates (EAGLE XG slim glass, Corning) (t = 0.5 mm) by the DC and RF sputtering technique. The ITO ceramic disk was used as a target for the ITO film growth at a power of 30 W in Ar pressure of 4 mTorr at room temperature by a commercial DC magnetron sputtering (KVS-2002, Korea Vacuum Tech, Korea). After patterning with the photolithography methods, the SZTO film was subsequently deposited at a power of 60 W by the RF magnetron sputtering technique (KVS-2004, Korea Vacuum Tech, Korea) in a mixed gas of Ar and O₂ at room temperature; the gas flow ratio of Ar and O₂ was set for 40:1 sccm. The as-deposited SZTO/ITO film was annealed at 500 °C for 2 h at ambient condition, and the detailed conditions for the target synthesis and the film growth were described in our earlier report [13]. A custom-made thermal evaporator was used for the deposition of the Cul films with the Cul powder (purity ≈99.998%) at room temperature on glass substrates (soda-lime glass for a microscope slide, Marienfeld) and SZTO/ITO/glass. For the fabrication of p-Cul/n-SZTO diodes, both Cul and Au/Ni films have been sequentially deposited with stencil masks that can produce 10 circular dots with a typical radius of 50 μm. The Au/Ni film (Figure 1a) was deposited to form ohmic contact between the Cul film and a tungsten probe tip; the Ni film (t = 5 nm) with a circular dot shape was first deposited on top of the Cul film, followed by the deposition of Au film (t = 50 nm) with the same circular dot size. It confirmed that two circular dots of the Au/Ni film grown on top of the Cul film exhibit linear behaviors in the current–voltage (I-V) curves by two tungsten probe tips connected to each dot (see, Figure S1). This implies that good ohmic contact was formed between Au/Ni films and Cul films as the p-type channel for a diode. Furthermore, the same measurements were performed with two tungsten probe tips connecting two respective circular dots of the ITO film grown on the SZTO film. It shows that good ohmic contact was formed between ITO and SZTO films as the n-type channel. The as-grown diodes were annealed at 50 °C for 125 h under the N₂ gas flowing condition of 20 mL/min. Optical transmittance and reflectance spectra measurements on the Cul/SZTO/ITO/glass were carried out by the UV-VIS-NIR spectrophotometer (Cary 5E, Varian). The crystallinity of films has been investigated by the θ-2θ scans in a high-resolution X-ray diffractometer (Empyrean™, PANalytical, Korea). The structural characterizations were conducted using atomic force microscopy (AFM) (NX10, Park Systems, Korea). The current density–voltage (I–V) characteristics of the diodes were investigated by the semiconductor parameter analyzer (4200-SCS, Keithley, Korea); all the measurements were performed under dark and air conditions at room temperature.

3. Results and Discussion

Figure 1a shows a schematic structure of the fabricated p-Cul/n-SZTO diode for electrical measurements, in which the SZTO film is grown on the ITO/glass, followed by the subsequent deposition of the circular Cul film and the metallic (Au/Ni) electrode. Figure 1b is an actual photograph of the Cul/SZTO/ITO/glass film without the Au/Ni layer, demonstrating that all the layers are transparent in the visible spectral range. The Cul/SZTO films (the orange dashed line) were deposited with a lateral size of 10 × 4 mm² on the ITO/glass substrate (the green dashed line); the thicknesses of the Cul, the SZTO, and the ITO films are 110, 27, and 50 nm, respectively. Hereafter, we denote the term Cul (x nm) as x nm-thick Cul film where x represents the thickness of the Cul film (tcul).
Figure 1. (a) A schematic structure of the p-CuI/n-SiZnSnO (SZTO) diode grown on the ITO deposited glass substrate, which was used for electrical characterization in this work. The CuI film of circular disk shape (with a diameter of 50 μm) were fabricated in two thicknesses of 140 and 20 nm while the thicknesses of SZTO and ITO films were 27 and 50 nm, respectively. Au/Ni (t = 50/5 nm) films were subsequently deposited on top of the CuI disk. (b) A separate film fabricated for optical characterization. The CuI(110 nm)/SZTO(27 nm) (the orange dashed line) were homogeneously deposited on top of the ITO/glass substrate (the green dashed line). All the regions exhibit clearly optical transparency. (c) Optical transmittance (T), reflectance (R), and absorption (A) spectra of the CuI (110 nm)/SZTO/ITO/glass sample shown in (b). The black solid line represents T1 of a glass substrate (t = 1 mm) only. (d) X-ray θ-2θ scan results of the CuI (110 nm)/SZTO/ITO/glass film shown in (b) and of another SZTO/ITO/glass film. The CuI film exhibits the preferential orientation of a (111) plane, and additional peaks represent a polycrystalline ITO film indicated as I.

Figure 1c exhibits the optical transmittance (T), reflectance (R), and absorption (A) spectra as a function of wavelength λ for the CuI/SZTO/ITO/glass (Figure 1b), and a black solid line represents T1 of a bare glass substrate. The absorbance is obtained from the relationship of A = 100−T−R, exhibiting small values less than 5% at λ ≥ 450 nm. The maximum T1 of the CuI/SZTO/ITO/glass is indeed found to be as high as ≥90% and is always larger than ≥80% in the visible spectral region (500–750 nm). In addition, the transmittance of the glass substrate T1,glass is a nearly constant of ≥90% (the black solid line). According to the relationship of T1, film = T1,measured/T1,glass, T1, film of the remaining films (CuI/SZTO/ITO) is then likely to be higher than ≥80% in the visible spectral region. All these results quantitatively demonstrate why the fabricated diode structure (CuI/SZTO/ITO/glass) maintains optical transparency, as shown in Figure 1b.

In addition, it is noteworthy that an exciton absorption peak is found at 407 nm (3.05 eV) (a gray dotted line in Figure 1c), as frequently observed in the CuI film [2,4,10,12]. Then, E_g of the CuI film is estimated as ≥3.1 eV from the relationship of E_g = E_{Z1,2} + E_{ex} where E_{Z1,2} is an exciton absorption energy of CuI and E_{ex} is an exciton binding energy of 62 meV [20]. The obtained E_g value is similar to our previous result (≥3.08 eV) [12] and other reports [2–4]. Based on the observation of the similar optical bandgap, the optical spectra are likely to be expected as high enough regardless of t_{CuI}, as confirmed in the
previous report [12]. Furthermore, the observation of such a sharp exciton absorption peak supports that the as-grown CuI film is of high quality.

The crystallinity of the as-grown films (CuI/SZTO/ITO/glass substrate) has been investigated by the X-ray $\theta$-2$\theta$ scan in Figure 1d. The CuI film exhibits a preferred orientation along the (111) plane, similar to the CuI/glass sample case (see, Figure S2 for the X-ray result). Since the nearest bottom layer is composed of an amorphous material, i.e., SZTO film or glass substrate, this (111) peak is unlikely to originate from the epitaxial CuI film [12]. It is well-known that the CuI system exhibits randomly oriented in-plane domains within the CuI (111) plane due to the low surface stability energy of the (111) plane [2]. The SZTO film cannot be identified in Figure 1d due to its amorphous nature, as confirmed by our previous transmission electron microscopy and X-ray photoelectron spectroscopy studies [21,22]. The extra peaks are the polycrystalline ITO film denoted as a symbol of $l$ in Figure 1d.

To investigate the electrical transport of the diodes before and after the N$_2$ annealing, we measured the $I$-$V$ curves of the diodes, which have the structure shown in Figure 1a using a two-point contact method. In this configuration, the two probe tips are connected to Au/Ni and ITO films for $p$-CuI and $n$-SZTO layers, respectively. Figure 2a shows the $I$-$V$ curve (black solid line) of the as-grown CuI (140 nm)/SZTO diode in a linear scale. A turn-on voltage ($V_{\text{turn-on}}$), which is the on-set voltage for a large increase in the current level, has been determined from a linear extrapolation of the $I$-$V$ curve in Figure 2a. The estimated $V_{\text{turn-on}}$ of the as-grown diode was 1.73 V. Figure 2b presents the corresponding $I$|$V$ curve in a semi-log scale. To extract the quantitative information on the diode parameters, we have tried to fit the data with the Shockley diode equation in the full range from $-2$ V to $+2$ V:

$$I(V) = I_s \left[ \exp \left( \frac{e(V - IR_s)}{\eta k_B T} \right) - 1 \right] + \frac{V - IR_s}{R_p} + I_o$$  \hspace{1cm} (1)

where $I_s$ is the reverse saturation current, $\eta$ is the ideality factor, $k_B$ is the Boltzmann constant, $T$ is the absolute temperature, $I_o$ is the offset current, $R_s$ is the series resistance, and $R_p$ is the parallel resistance [11]. The orange lines in Figure 2b represent the curve fitting results, which indeed well explain the measured data except for the irreversible charge trap effect near 0.8 V. We will discuss the resultant parameters in Figure 3.
Similarly, the measured $I-V$ and $|j|V$ curves in the annealed CuI (140 nm)/SZTO diode are plotted as red solid lines in Figure 2c,d, respectively. The green dashed line of the $|j|V$ curve represents the curve fitting result. What is most conspicuous in the behavior of the annealed diode is the decrease (increase) of the current level in the negative (positive) bias region. This immediately points out that the current rectification ratio $I/R_s$, where $I$ is the current value at $+2 \text{ V}$ and $R_s$ is the current at $-2 \text{ V}$, is enhanced after the annealing. As the SZTO layer is expected to be stable at the annealing condition (50 °C, 125 h), to understand the enhancement of $I/R_s$, one should understand first how the annealing process will affect the properties of CuI film. It is known that in the as-grown CuI film, $V_{Cu}$ is likely to exist, behaving as a dominant acceptor source and also as an ionized impurity scattering source. Upon the ex situ thermal annealing at 50 °C being performed for 125 h, iodine vacancies ($V_I$) can be additionally created, thereby compensating the native $V_{Cu}$. In addition to $V_{Cu}$ compensation by $V_I$, thermal energy can provide extra energy for rendering the migration of existing Cu vacancies from the inside of the CuI film to the outside of the surface or grain boundary [3]. Therefore, the optimal thermal annealing can lead to suppression of ionized impurity scattering via the compensation of $V_{Cu}$ by $V_I$ and also by the reduction of $V_{Cu}$ inside the CuI film. At the same time, a reduction of structural defects near the grain boundaries of the CuI film is also expected, which in turn can form a smooth and uniform interface to improve the $pn$ diode

\[ V_{\text{turn-on}} = 1.73 \text{ V} \]

\[ V_{\text{turn-on}} = 1.74 \text{ V} \]
performance. Reduced grain boundaries after annealing can be verified in the AFM image of the CuI film/glass in Figure S3.

Several pieces of evidence supporting improved diode performance after annealing can be found in the I-V (or |j|1-V) characteristics in Figure 2c,d; the hysteresis of the |j|1-V curve between the forward and reverse sweeping directions decreases, 𝑉_{𝑡𝑢𝑛−𝑜𝑛} slightly increases from 1.73 to 1.74 V, the offset current 𝐼₀ decreases in the flat range from ~2 to ~0.7 V, and the |j|1-V curve produces significant noise in the flat region. To better understand microscopically how the diode performance improves, we discuss here the supporting evidence in more detail. First, it should be reminded that irreversible charge traps mainly cause the diode hysteresis because the charged trap sites, such as 𝑉_{𝐶𝑢}, act as a slowly responding component under external voltage bias. Thus, the decreased hysteresis in the |j|1-V curve demonstrates that the charged trap sites have been greatly reduced.

Second, the slight increase of 𝑉_{𝑡𝑢𝑛−𝑜𝑛} from 1.73 to 1.74 V also supports the improved diode performance. A threshold voltage (𝑉_𝑡ℎ), which is an ideal voltage to begin the current flow, is expected to become fairly high in this diode; it is expressed by 𝑉_{𝑡ℎ−𝑝} = 𝑉_𝑡ℎ + |Δ𝐸_𝑉/𝑒| for a p-type carrier and by 𝑉_{𝑡ℎ−𝑛} = 𝑉_𝑡ℎ + |Δ𝐸_𝐶/𝑒| for an n-type carrier, where 𝑉_𝑡ℎ is the built-in potential of a diode, Δ𝐸_𝑉 is the valence band offset, and Δ𝐸_𝐶 is the conduction band offset between two semiconductors [2]. Based on the band diagram of the CuI/SZTO diode (vide infra, Figure 5), it turns out to be 𝑉_𝑡ℎ = 0.99 V, |Δ𝐸_𝑉/𝑒| = 2.55 V, and |Δ𝐸_𝐶/𝑒| = 1.90 V, resulting in 𝑉_{𝑡ℎ−𝑝} = 3.54 V for the injection of holes from p-CuI to n-SZTO and 𝑉_{𝑡ℎ−𝑛} = 2.89 V for the injection of electrons from n-SZTO to p-CuI. Thus, it is likely that electron injection is more probable than hole injection because the absolute conduction band offset |Δ𝐸_𝐶/𝑒| is 0.66 V less than |Δ𝐸_𝑉/𝑒|. The obtained 𝑉_{𝑡𝑢𝑛−𝑜𝑛} = 1.74 V in Figure 2c for the annealed diode is obviously smaller than the predicted 𝑉_{𝑡ℎ−𝑛} = 2.89 V. Since the 𝑉_{𝐶𝑢} creates an intermediate state that can form an additional current path at the diode interface, the actual 𝑉_{𝑡𝑢𝑛−𝑜𝑛} should be lower than 𝑉_𝑡ℎ in general. Therefore, in turn, the increased 𝑉_{𝑡𝑢𝑛−𝑜𝑛} after annealing indicates reduced extra leakage current paths by the decrease of 𝑉_{𝐶𝑢} or by the compensation of 𝑉_{𝐶𝑢}.

Finally, the reduced 𝐼₀ after annealing also supports the improved diode performance. 𝐼₀ can be generated by other leakage sources irrelevant to the bias voltage such as instrumental effects or pinholes that can exist across two electrodes. Once 𝐼₀ was formed at a diode, it appears as a constant current in the flat region of the |j|1-V curve; for instance, the 𝐼₀ level is ~5.9 pA in the bias range from ~2 to ~0.7 V in Figure 2b. Therefore, the reduced 𝐼₀ level from 5.9 to 1.1 pA after the annealing in Figure 2d indicates that such a side effect has been mitigated by the annealing, too. As the 𝐼₀ decreased after annealing, the current noise in the negative bias range concurrently increased. It implies that the actual current is small enough to reach the resolution limit of the instrument (Keithley 4200-SCS, ±1 pA).

Figure 3 compares all the obtained diode parameters for both CuI (20 nm)/SZTO and CuI (140 nm)/SZTO diodes before and after annealing. Here, we remind the physical meaning of each diode parameter except for 𝐼_𝑠/𝐼_𝑛 and 𝐼₀ already explained above. 𝐼_𝑠 represents the reverse saturation current, which occurs by the minority carriers located at the depletion region of a pnn diode. 𝜂 describes a diode transport model; 𝜂 is known to change by diffusion (𝜂 = 1), recombination (𝜂 = 2), and numerous defects region (𝜂 > 2). 𝑅_𝑛 is determined by the contact resistance of several junctions between two films and between the electrode/film, and 𝑅_𝑝 represents the parasitic parallel resistance formed by an additional leakage path. In the case of the CuI (140 nm)/SZTO diode, the annealing process results in the increase of 𝐼_𝑠/𝐼_𝑛 from 2.7 × 10⁶ to 6.6 × 10⁷ by ~25 times, the decrease of 𝐼₀ from 5.9 to 1.1 pA, the nearly same 𝐼₀ being a quite low level of ~0.07 fA, the decrease of 𝜂 from 2.96 to 2.66, the decrease of 𝑅_𝑛 from 6.1 to 3.9 kΩ, and the slight increase of 𝑅_𝑝 from ~2 to ~5 TΩ shown in Figure 3.
The thermal annealing process, as explained in Figure 2, is likely to induce several physical processes; (1) the decrease of charged trap sites by $V_{Cu}$, (2) a reduction of grain boundaries from the out-diffusion of $V_{Cu}$, and (3) a reduced ionized impurity scattering with reduced $p$-type carriers (see, Figure S5 for the Cul/glass Hall effect results). All the processes (1)–(3) can result in a decreasing tendency, as observed in the parameters $I_o$ and $R_s$. The decrease of $I_o$ implies that other leakage sources such as the pinholes across two electrodes are reduced as a result of reduced vacancies, $p$-type carriers, and grain boundaries. Furthermore, with reduced grain boundaries, the contract resistance $R_s$ between the Cul and the Au/Ni film is likely reduced, too. In addition, the $\eta = 2.96$ before annealing (Figure 3d) suggests the presence of numerous defects at the diode depletion region. Thus, the decrease of $\eta$ from 2.96 to 2.66 after thermal annealing suggests reduced $V_{Cu}$ and improved diode interface to become more homogeneous. The increase of $R_s$ by $\approx 3$ TΩ, albeit having a large least square fitting error close to the instrumental measurement limit, is also consistent with the reduced $V_{Cu}$. The thermal annealing did not affect the saturation current, producing the nearly same value of $I_s = \approx 0.07$ fA, which is close to the instrumental resolution limit. This implies that $I_s = \approx 0.07$ fA is indeed close to an ideal value expected in this diode configuration. All the positive effects reflected in those parameters in Figure 3b–f after the annealing process coherently explains why $I/I_0$ has been improved by $\approx 25$ times from $2.7 \times 10^6$ to $6.6 \times 10^7$ in the Cul (140 nm)/SZTO diode (Figure 3a).

To compare how the annealing can affect the characteristics of the diode made of a thinner Cul film, we have similarly studied the electrical properties of the Cul (20 nm)/SZTO diode before and after applying the same thermal annealing conditions, of which $I-V$ ($I-j-V$) curves are provided in Figure S6. All the parameters obtained from the curve fitting results based on Equation (1) are also summarized in Figure 3; in the Cul (20 nm)/SZTO diode, the thermal annealing results in the decrease of $I_o$ from $\approx 4.5$ to 1.2 pA, the decrease of $I_s$ from 20.5 fA to 0.20 fA, the decrease of $\eta$ from 3.89 to 3.15, and the nearly

Figure 3. Summary of various diode parameters; (a) current rectification ratio $I/I_0$; (b) offset current $I_o$; (c) reverse saturation current $I_s$; (d) ideality factor $\eta$; (e) series resistance $R_s$, and (f) parallel resistance $R_p$. Black and red colors represent the data of the as-grown and annealed diode, respectively. All the parameters are estimated by fitting the results in Figure 2b,d with Equation (1). Error bars in (f) represent the least square fitting error. Error bars from the least square fitting were less than 5% for the other parameters (b–e).
same of $R_p$ of $\approx 4$ TΩ. The initial values of $I_s$ and $\eta$ after the growth seem to be all larger than the corresponding values in the CuI (140 nm)/SZTO diode, while $I_s$ and $R_p$ are comparable. This indicates that the contribution of $V_{Cu}$ and related grain boundaries are larger in the thin (20 nm) films to cause the numerous defect regime in the diode, i.e., $\eta = 3.89$. After annealing, all the parameters of $I_s$, $I_v$, and $\eta$ exhibit improvement, as similarly observed in the thick diode. Therefore, the thermal annealing seems to be also effective in improving the physical properties of the CuI (20 nm) film by reducing $V_{Cu}$, grain boundaries, and ionized impurity scattering.

The most notable difference between the CuI (20 nm) and the CuI (140 nm) diode is found in the variation of $R_s$ and $I_s/I_v$ after annealing. $R_s$ increases from 95.8 to 133 kΩ, while $I_s/I_v$ exhibits a slight increase from $5.5 \times 10^5$ to $2.4 \times 10^6$. Note that $I_0(+2V)/I_0(-2V)$ was calculated from the fitting curves in this case to avoid the noise-induced errors in the estimation of $I_0(-2V)$. In general, $R_s$ is a main limiting factor for $I_v$, as the forward bias voltage dropped by the interface contact resistance; $I_v$ is supposed to decrease, being roughly proportional to $R_s$. Therefore, the moderate increase of $I_s/I_v$ by a factor of $\approx 4$ in the CuI (20 nm) diode, as compared with the factor of $\approx 25$ increase in the CuI (140 nm) diode should be mainly attributed to the unexpected increase of $R_s$. Without the deterioration of $R_s$, the improvements of the other parameters $I_s$, $I_v$, and $\eta$ should have produced much more enhanced $I_s/I_v$. The undesirable increase of $R_s$ upon annealing indicates that the CuI (20 nm) film just starts to degrade due to the formation of a large amount of $V_t$. The thermal degradation of the CuI has been known in the thin films with $t_{CuI} < 100$ nm [3] and even in a crystal [23]. If the CuI is subject to excessive thermal annealing, out-diffusion of $V_{Cu}$ and the excessive formation of $V_t$ can give rise to degradation in the physical properties of CuI; it becomes porous, exhibits yellowish-brown colors, and eventually develops many cracks [3]. Therefore, for a very thin film limit of $t_{CuI} < 100$ nm, it is expected that a shorter time or a lower temperature for annealing might be suitable to achieve a higher $I_s/I_v$. Thus, our results indicate that an optimal annealing condition should be carefully searched for each thin film with a different thickness.

It is emphasized that $I_s/I_v = 6.6 \times 10^6$ is quite a high value among the heterojunction diodes consisting of the $p$-CuI film. Figure 4 compares $I_s/I_v$ of the $p$-CuI/$n$-SZTO diodes with those of other CuI-based transparent heterojunction diodes that have a high $I_s/I_v > 10^7$; $2 \times 10^7$ at $\pm 2$ V for $p$-CuI/$n$-ZnO (a polycrystalline CuI film) [2], $2 \times 10^8$ at $\pm 2$ V for $p$-CuI/$n$-ZnO (an epitaxial CuI film) [11], $7 \times 10^8$ at $\pm 2$ V for $p$-CuI/$n$-BaSnO₃ [12], $6 \times 10^8$ at $\pm 2$ V for $p$-CuI/$n$-IGZO [3], and $10^9$ at $\pm 1.5$ V for $p$-CuI/Bi/n-IGZO (x = 0.0 − 1.0) [10]. Albeit the highest value of $I_s/I_v = 2 \times 10^8$ realized in the $p$-CuI/$n$-ZnO diode is higher than that of the present $p$-CuI/$n$-SZTO diode by $\approx 30$ times, to realize such a diode requires a special growth condition, i.e., an epitaxial growth of the CuI film on top of an epitaxial ZnO film. This implies that such a high $I_s/I_v$ is hard to achieve in a flexible device. Although the $I_s/I_v = 1 \times 10^9$ in the $p$-CuI/$n$-IGZO diodes looks also higher than that of the $p$-CuI/$n$-SZTO diode, a proper comparison of $I_s/I_v$ might be required as the work used the measured $I_s$ and the fitted $I_v$ [10].
To quantitatively compare the performance of various diodes made of the p-type CuI and n-type materials, several diode parameters and photo-response results are also summarized in Table 1. The main parameter that characterizes the one-way electrical transport of a diode is \( I_l/I_s \). Most of the diode exhibit \( I_l/I_s \) larger than \( \approx 7 \times 10^5 \) except recent two devices with rather large interface areas as they focus on the increase of photocurrent in the \( pn \) diode [9,19]. The ideality factor \( \eta \) seems to be lower than 2 when the \( n \)-type materials are epi-films of ZnO or amorphous IGZO film while the \( \eta \) of the p-CuI/n-SZTO is as large as 2.7–3.0, indicating that disorder effects in the CuI film can be further reduced by better annealing or growth conditions. The \( I_s \) of the p-CuI/n-SZTO diode is much lower than those of the p-CuI/n-ZnO and the p-CuI_{1-x}Br_{x}/n-IGZO diodes due to the inclusion of offset current in the fitting process. The \( R_s \) value of the p-CuI/n-SZTO is still higher than those of other diodes, leaving rooms for improvement by reducing interface resistance at the \( pn \) junction and p- or n-type films/electrodes. Therefore, if the \( R_s \) and the \( \eta \) can be further improved in the p-CuI/n-SZTO, the \( I_l/I_s \) is likely to be enhanced more. Finally, in Table 1, to illustrate a direction of future applications, we have also listed several recent cases where the photo responsivity has been tested in the transparent \( pn \) diode made of the p-CuI. Based on these recent related studies, it is expected that flexible, optically transparent, cheap UV photodetectors can be fabricated by the p-CuI/n-SZTO diode.
Table 1. Summary of diode parameters for various different \(pn\) junctions, consisting of the \(p\)-type CuI.

| \(pn\) Diode                  | Current Rectification Ratio \(I_v/I_s\) | Saturation Current (A) \(I_s\) | Ideality Factor \(\eta\) | Series Resistance (\(\Omega\)) \(R_s\) | Parallel Resistance (\(\Omega\)) \(R_p\) | Responsivity (Wavelength) (mA W\(^{-1}\)) |
|-------------------------------|----------------------------------------|---------------------------------|-------------------------|-------------------------------------|-------------------------------------|-----------------------------------|
| pc-CuI/epi-ZnO [2]           | \(2 \times 10^7 \pm 2 \text{ V}\)     | \(1.3 \times 10^{-11}\)        | 1.7                     | \(2.9 \times 10^2\)                 | \(\geq 10^{12}\)                    | -                                 |
| pc-CuI/epi-ZnO [2]           | \(4 \times 10^7 \pm 2 \text{ V}\)     | \(6.2 \times 10^{-15}\)        | 1.6                     | \(2.0 \times 10^2\)                 | \(\geq 10^{12}\)                    | -                                 |
| pc-CuI/epi-ZnO [2]           | \(2 \times 10^7 \pm 2 \text{ V}\)     | \(3.2 \times 10^{-13}\)        | 1.8                     | \(2.5 \times 10^2\)                 | \(\geq 10^{12}\)                    | -                                 |
| epi-CuI/epi-ZnO [11]         | \(2 \times 10^9 \pm 2 \text{ V}\)     | \(1.1 \times 10^{-12}\)        | 1.7                     | \(1.7 \times 10^2\)                 | \(3 \times 10^{12}\)                | -                                 |
| pc-CuI/epi-BaSnO\(_3\) [12]   | \(7 \times 10^5 \pm 2 \text{ V}\)     | \(9.9 \times 10^{-13}\)        | 1.5                     | \(-5.5 \times 10^2\)                | \(2 \times 10^9\)                   | -                                 |
| pc-CuI/a-InGaZnO [3]         | \(6 \times 10^6 \pm 2 \text{ V}\)     | -                               | 1.6                     | \(2.0 \times 10^2\)                 | -                                   | 0.3 (365 nm)                      |
| pc-CuI\(_{x}\)Br\(_{y}\)/a-InGaZnO [10] | \(\sim 2 \times 10^9 \pm 1.5 \text{ V}\) | \(\sim 2 \times 10^{-12}\)     | 1.9                     | -                                   | -                                   | -                                 |
| np-CuI/sc-CsPbBr\(_3\) [9]  | \(3 \times 10^2 \pm 2 \text{ V}\)     | -                               | -                       | -                                   | -                                   | 1.4 (540 nm)                      |
| pc-CuI/sc-Ga\(_2\)O\(_3\) [19] | \(6 \times 10^3 \pm 2 \text{ V}\)     | -                               | 3.7                     | -                                   | -                                   | 2.49 (254 nm)                     |
| pc-CuI(20 nm)/a-SiZnSnO (this work) | \(2 \times 10^6 \pm 2 \text{ V}\)     | \(2.0 \times 10^{-16}\)        | 3.2                     | \(1.3 \times 10^5\)                 | \(3 \times 10^{12}\)                | -                                 |
| pc-CuI(140 nm)/a-SiZnSnO (this work) | \(7 \times 10^7 \pm 2 \text{ V}\)     | \(0.7 \times 10^{-16}\)        | 2.7                     | \(3.9 \times 10^3\)                 | \(5 \times 10^{12}\)                | -                                 |

* epi: epitaxial film, pc: polycrystalline film, sc: single crystal, a: amorphous, np: nanoparticle.

Figure 5a compares the energy band alignment of several wide bandgap materials, including CuI [2,12], SZTO [13,22], IGZO [8,24], BaSnO\(_3\) [12,25], and ITO [26]. Based on the experimental results from previous reports, the band energies of these materials are aligned at the vacuum energy level \(E_{\text{vac}} = 0\). The top (red) and bottom (blue) columns present conduction and valance bands, respectively. In order to investigate the energy band diagram of the annealed CuI (140 nm)/SZTO diode shown in Figure 5b, first of all, several energies such as \(E_{\text{vac}}\), valance band maximum (\(E_V\)), and conduction band minimum (\(E_C\)) are determined from Figure 5a. Subsequently, the Fermi energy level (\(E_F\)) is calculated from the Anderson diode model for heterojunction [27]; various input parameters of valance band maximum \(E_V\), conduction band minimum \(E_C\), dielectric constant [22,22], and effective masses [22,28] of both CuI and SZTO are adopted from the literature. \(E_g\) and \(n\) of SZTO are estimated from our previous work [13], while \(E_g\) and \(p\) of CuI are obtained in this work. Basic parameters and related references are summarized in Table 2.
The resultant band diagram is consistent with the type-II band alignment (or staggered gap type), in which $E_c$ of the $n$-type material is located at the energy window between $E_c$ and $E_V$ of the $p$-type material. The predicted $eV_h$, the depletion width of Cul, and the depletion width of SZTO are found as 0.99 eV, 0.03 nm, and 37.1 nm, respectively. The present Cul/SZTO diode is indeed the one-side abrupt junction, of which the depletion region is mostly formed at, in this case, the SZTO layer. It is noted that the $n$-type depletion width of 37.1 nm is larger than the thickness of the SZTO film itself (27 nm). In this condition, an effective negative bias might be formed at the interface, and consequently, a finite forward bias should be required to reduce the electric field and to start the current flow across the $pn$ diode. Consistent with this scenario, relatively high voltages for the current onset in the $Ij$-$V$ curves have been indeed found at $\approx$0.7 V in Figure 2b,d.

Table 2. Input parameters of the Anderson heterojunction diode model for the annealed $p$-Cul/$n$-SiZnSnO (SZTO) diode where $m_o$ is the electron mass.

| Film    | Bandgap (eV) | Electron Affinity (eV) | Carrier Density (cm$^{-3}$) | Dielectric Constant | Effective Mass |
|---------|--------------|------------------------|-----------------------------|---------------------|----------------|
| $p$-Cul | 3.1          | $\sigma$2.5            | $9.4 \times 10^{18}$        | $\sigma$5.1         | $\sigma$1.4$m_o$ |
| $n$-SZTO| 3.7          | $\sigma$4.4            | $6.8 \times 10^{15}$        | $\sigma$4.75        | $\sigma$0.2$m_o$ |

$^a$Ref. [2], $^b$Ref. [28], $^c$Ref. [13], $^d$Ref. [22].

4. Conclusions

We have studied the electrical characteristics of transparent $p$-Cul/$n$-SiZnSnO (SZTO) heterojunction diodes with a variation of Cul film thicknesses (20 nm and 140 nm), for which thermal evaporation and RF magnetron sputtering techniques have been utilized to deposit the (111) oriented Cul and amorphous SZTO films, respectively. Upon applying a thermal annealing condition of 125 h at 50 °C under N$_2$ gas atmosphere, we have found that the current rectification ratio $(I_h/I_s)$ is enhanced by $\approx$25 times up to $6.6 \times 10^7$ in the thick Cul (140 nm)/SZTO diode due to the improvement of all the diode parameters as
systematically obtained by the curve fitting to the Shockley diode equation. On the other hand, the thin Cul (20 nm)/SZTO diode exhibits a moderate increase of \( I_n/I_s \) by \( \approx 4 \) times up to \( 2.4 \times 10^6 \) due to the increase of contact resistance of the electrode. Changes of the diode parameters with a variation of the p-Cul film thickness or by the thermal annealing and their physical implications have been discussed in the two kinds of the transparent p-Cul/n-SZTO diode. Based on the comparison with the energy band alignment of various semiconductors, we have proposed the realization of the type-II band diagram in the p-Cul/n-SZTO diode. The present p-Cul/n-SZTO diode can be potentially used as a valuable transparent component in various optoelectronic applications such as a light-emitting diode or a UV photodetector.

**Supplementary Materials:** The following are available online at www.mdpi.com/2079-4991/11/5/1237/s1, Figure S1: Current-voltage curves for \( p- \) and \( n \)-type films to check ohmic contact. Figure S2: Structural properties of Cul films on glass substrates measured by the high-resolution X-ray diffractometer. Figure S3: AFM images of Cul films on glass substrates before and after thermal annealing. Figure S4: Surface topography images of Cul/glass, SZTO/ITO/glass, and Cul/SZTO/ITO/glass measured by AFM. Figure S5: Hall effect results as a function of the thickness of Cul films on glass substrates. Figure S6: The current–voltage and the current density–voltage curves measured by the semiconductor analyzer in the Cul (20 nm)/SZTO diode before and after the Ni annealing.

**Author Contributions:** J.H.L. carried out diode fabrication, characterization, analysis, and manuscript writing. B.H.L. provided specimens and experimental data. J.K. supported scientific discussions of overall results. M.D. contributed to characterization. K.J. and C.J. collaborated and provided resources. S.Y.L. and K.H.K. supervised and proposed the experiments. All authors have read and agreed to the published version of the manuscript.

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**References**

1. Chen, D.; Wang, Y.; Lin, Z.; Huang, J.; Chen, X.Z.; Pan, D.; Huang, F. Growth Strategy and Physical Properties of the High Mobility P-Type Cul Crystal. *Cryst. Growth Des.* 2010, 10, 2057–2060.

2. Grundmann, M.; Schein, F.-L.; Lorenz, M.; Bontgen, T.; Lenzner, J.; von Wenc stern, H. Cuprous Iodide—A p-type Transparent Semiconductor: History and Novel Applications. *Phys. Status Solidi A* 2013, 210, 1671–1703.

3. Yamada, N.; Kondo, Y.; Ino, R. Low-Temperature Fabrication and Performance of Polycrystalline Cul Films as Transparent P-Type Semiconductors. *Phys. Status Solidi A* 2018, 216, 1700782.

4. Zi, M.; Li, J.; Zhang, Z.; Wang, X.; Han, J.; Yang, X.; Zhi, Z.; Gong, H.; Ji, Z.; Cao, B. Effect of Deposition Temperature on Transparent Conductive Properties of Cul Film Prepared by Vacuum Thermal Evaporation. *Phys. Status Solidi A* 2015, 212, 1466–1470.

5. Jeon, K.; Jee, H.; Park, M.J.; Lim, S.; Jeong, C. Characterization of the Copper Iodide Hole-Selective Contact for Silicon Solar Cell Application. *Thin Solid Films* 2018, 660, 613–617.

6. Baek, S.-D.; Kwon, D.-K.; Kim, Y.C.; Myoung, J.-M. Violet Light-Emitting Diodes Based on p-Cul Thin Film/n-MgZnO Quantum Dot Heterojunction. *ACS Appl. Mater. Interfaces* 2020, 12, 6037–6047.

7. Lee, H.J.; Lee, S.; Ji, Y.; Cho, K.G.; Choi, K.S.; Jeon, C.; Lee, K.H.; Hong, K. Ultrahigh-Mobility and Solution-Processed Inorganic P-Channel Thin-Film Transistors Based on a Transition-Metal Halide Semiconductor. *ACS Appl. Mater. Interfaces* 2019, 11, 40243–40251.

8. Yamada, N.; Kondo, Y.; Cao, X.; Nakano, Y. Visible-Blind Wide-Dynamic-Range Fast-Response Self-Powered Ultraviolet Photodetector Based on Cul/In-Ga-Zn-O Heterojunction. *Appl. Mater. Today* 2019, 15, 153–162.

9. Zhang, Y.; Li, S.; Yang, W.; Joshi, M.K.; Fang, X. Millimeter-Sized Single-Crystal CsPbBr3/Cul Heterojunction for High-Performance Self-Powered Photodetector. *J. Phys. Chem. Lett.* 2019, 10, 2400–2407.

10. Yamada, N.; Tanida, Y.; Murata, H.; Kondo, T.; Yoshida, S. Wide-Range-Tunable p-Type Conductivity of Transparent Cul–Br Alloy. *Adv. Funct. Mater.* 2020, 30, 2003096.

11. Yang, C.; Kneiß, M.; Schein, F.-L.; Lorenz, M.; Grundmann, M. Room-temperature Domain-epitaxy of Copper Iodide Thin Films for Transparent Cul/ZnO Heterojunctions with High Rectification Ratios Larger than 10. *Sci. Rep.* 2016, 6, 21937.
12. Lee, J.H.; Lee, W.-J; Kim, T.H.; Lee, T.; Hong, S.; Kim, K.H. Transparent p-Cul/\(n\)-BaSnO\(_3\) Heterojunctions with a High Rectification Ratio. J. Phys. Condens. Matter 2017, 29, 384004.
13. Lee, B.H.; Cho, K.-S.; Lee, D.-Y.; Sohn, A.; Lee, J.Y.; Cho, H.; Park, S.; Kim, S.-W.; Kim, S.; Lee, S.Y. Investigation on Energy Bandgap States of Amorphous SiZnSnO Thin Films. Sci. Rep. 2019, 9, 19246.
14. Lee, B.H.; Sohn, A.; Kim, S.; Lee, S.Y. Mechanism of Carrier Controllability with Metal Capping Layer on Amorphous Oxide SiZnSnO Semiconductor. Sci. Rep. 2019, 9, 886.
15. Haynes, W.M.; Lide, D.R.; Bruno, T.J. CRC Handbook of Chemistry and Physics: A Ready-Reference Book of Chemistry and Physical Data, 95th ed.; CRC Press LLC: Boca Raton, FL, USA, 2014; pp. 65–70.
16. Chen, J.; Ouyang, W.; Yang, W.; He, J.-H.; Fang, X. Recent Progress of Heterojunction Ultraviolet Photodetectors: Materials, Integrations, and Applications. Adv. Funct. Mater. 2020, 30, 1909909.
17. Cao, F.; Jin, L.; Wu, Y.; Ji, X. High-Performance, Self-Powered UV Photodetector Based on Au Nanoparticles Decorated ZnO/Cul Heterostructure. J. Alloys Compd. 2021, 859, 158383.
18. Li, S.; Zhang, Y.; Yang, W.; Fang, X. Solution-Processed Transparent Snt\(^{\text{+}}\)-Doped Cul Hybrid Photodetectors with Enhanced Performances. Adv. Mater. Interfaces 2019, 6, 1900669.
19. Ayhan, M.E.; Shinde, M.; Todankar, B.; Desai, P.; Ranade, A.K.; Tanemura, M.; Kalita, G. Ultraviolet Radiation-Induced Photovoltaic Action in \(y\)-Cul/\(\beta\)-Ga:O heterojunction. Mater. Lett. 2020, 262, 127074.
20. Sauder, T.; Daunois, A.; Deiss, J.L.; Merle, J.C. Effects of Uniaxial Stress on the Excitons in Single Crystals of Cul: Comparison with Thin Films. Solid State Commun. 1984, 51, 323–326.
21. Lee, B.H.; Hong, S.-Y.; Kim, D.-H.; Kim, S.; Kwon, H.-I.; Lee, S.Y. Investigation on Trap Density Depending on Si Ratio in Amorphous SiZnSnO Thin-Film Transistors. Phys. B Condensed Matter 2019, 574, 311629.
22. Chong, E.; Kang, I.; Park, C.H.; Lee, S.Y. First-Principle Study of Amorphous SiZnSnO Thin-Film Transistor with Excellent Stability. Thin Solid Films 2013, 534, 609–613.
23. Gruzintsev, A.N.; Zagorodnev, V.N. Temperature-Dependent Conductivity and Photoconductivity of p-Cul Crystals. Semiconductors 2012, 46, 35–40.
24. Lee, K.; Nomura, K.; Yanagi, H.; Kamiya, T.; Ikenaga, E.; Sugiyama, T.; Kobayashi, K.; Hosono, H. Band Alignment of InGaZnO/Si Interface by Hard X-ray Photoelectron Spectroscopy. J. Appl. Phys. 2012, 112, 033713.
25. Lee, W.-J.; Kim, H.J.; Kang, J.; Jang, D.H.; Kim, T.H.; Lee, J.H.; Kim, K.H. Transparent Perovskite Barium Stannate with High Electron Mobility and Thermal Stability. Annu. Rev. Mater. Res. 2017, 47, 391–423.
26. Liu, T.; Zhang, X.; Zhang, J.; Wang, W.; Feng, L.; Wu, L.; Li, W.; Zeng, G.; Li, B. Interface Study of ITO/ZnO and ITO/SnO: Complex Transparent Conductive Layers and Their Effect on CdTe Solar Cells. Int. J. Photoenergy 2013, 2013, 765938.
27. Chuang, S.L. Physics of Optoelectronic Devices; Wiley: New York, NY, USA, 1995; pp. 21–80.
28. Yu, C.I.; Goto, T.; Ueta, M. Emission of Cuprous Halide Crystals at High Density Excitation. J. Phys. Soc. Jpn. 1973, 34, 693–698.