

Defect engineering-induced Seebeck coefficient and carrier concentration decoupling in CuI by noble gas ion implantation

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Copper(I) iodide, CuI, is the leading *p*-type non-toxic and earth-abundant semiconducting material for transparent electronics and thermoelectric generators. The power factor of CuI thin films was increased from $332 \pm 32 \mu\text{Wm}^{-1}\text{K}^{-2}$ to $578 \pm 58 \mu\text{Wm}^{-1}\text{K}^{-2}$ after implantation with noble gas ions (Ne, Ar, Xe). The increased power factor is due to a decoupling of the Seebeck coefficient and carrier concentration identified through a changing scattering mechanism. Ion implantation causes the abundant production of Frenkel pairs, which were found to suppress compensating donors in CuI, studied using density functional theory calculations. The compensating donor suppression led to a significantly improved Hall carrier concentration, increasing from $6.5 \times 10^{19} \pm 0.1 \times 10^{19} \text{cm}^{-3}$ to $11.5 \times 10^{19} \pm 0.4 \times 10^{19} \text{cm}^{-3}$. This work provides an important step forward in the development of CuI as a transparent conducting material for electronics and thermoelectric generators by introducing beneficial point defects with ion implantation.

Energy harvesting through the thermoelectric effect is a rapidly growing low carbon-emission technology. Materials facilitating such energy conversion are becoming increasingly technologically important¹. Thermoelectric devices convert heat flux into electrical power by the Seebeck effect at a conversion efficiency which depends on the figure of merit $ZT = \alpha^2 \sigma T / \kappa$ where α , σ , κ , and T are the Seebeck coefficient, electrical conductivity, total thermal conductivity, and absolute temperature, respectively². The highest-performing room temperature thermoelectric materials are degenerately doped semiconductors, usually with small band gaps, such as the tetradymite alloys based on $(\text{Bi,Sb})_2(\text{Te,Se})_3$ composition, with up to $ZT = 1.5$. Unfortunately, these compounds are composed of expensive and toxic precursors^{2,3}. Heavily doped wide band gap semiconductors provide a much wider application scope than their non-transparent counterparts⁴. This advantage is particularly useful at room temperature, but, before device integration can be considered on grounds of cost-effectiveness, an increase in performance is still required.

The state of the art *n*-type transparent conductors for near room-temperature thermoelectric applications are $\text{In}_2\text{O}_3:\text{Sn}$ and $\text{ZnO}:\text{Al}$, each with electrical conductivities near $\sigma \sim 10000 \text{Scm}^{-15}$, whilst for *p*-type conductors, CuI possesses a moderate conductivity of $\sigma \sim 100 \text{Scm}^{-16,7}$. The other *p*-type transparent conductors are doped copper oxides, the best of which is CuAlO_2 with $\sigma = 0.01 \text{Scm}^{-18}$. The reason for the conductivity

difference is the high hole mobility in CuI, believed to possibly to reach $30 \text{cm}^2\text{V}^{-1}\text{s}^{-1}$ at carrier concentrations of 10^{20}cm^{-39} . Presently, hole mobilities are limited to $\approx 10 \text{cm}^2\text{V}^{-1}\text{s}^{-1}$ at carrier concentrations near 10^{20}cm^{-3} . The high carrier mobilities in-part originate from the band-degenerated light and heavy hole bands with effective masses $0.3m_0$ and $2.4m_0$, where m_0 is the free electron mass¹⁰. The capability for CuI as a functional material has already been demonstrated in laboratory scale components such as in thin film transistor^{11,12}, optical memory element^{13,14}, and as *p*-type legs of transparent thermoelectric generator^{6,15,16} applications, the performance of which in one way or another relies on a high electrical conductivity. Further investigation of its properties and improvements in electrical conductivity toward 1000Scm^{-1} will likely follow with commercial applications in commonplace electronic devices. The further advantages of CuI over alternative *p*-type transparent conductors is its non-toxic and earth-abundant constituents in addition to its facile fabrication procedures⁶.

Ion implantation is an alternative method to annealing by which to modify the electrical and thermal properties of a thin film or the surface of a bulk material chemically or structurally. Ion implantation has seen recent interest for thermoelectric material thin films, especially the case of ScN^{17-19} or $\text{Bi}_2\text{Te}_3^{20,21}$ for nanostructuring and chemical doping. Ion implantation is an energetic process which displaces atoms from their lattice sites into interstitial sites and antisites in a collision cascade, leading to the formation of a large concentration of Frenkel pairs within a small volume. The displacement of atoms from their lattice sites usually reduces the phonon thermal conductivity as the long-range crystal order is sup-

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TABLE I. Relationship between implantation fluence F , displacements per ion D , and (70 nm) depth-averaged DPA.

Species	Energy [keV]	F [ions cm ⁻²]	D [disp. ion ⁻¹]	DPA
Ne	13	0	200	0
Ne	13	1.6×10^{15}	200	1.3
Ne	13	3.2×10^{15}	200	2.5
Ne	13	9.6×10^{15}	200	7.4
Ne	13	1.92×10^{16}	200	14.1
Ar	27	0	442	0
Ar	27	7.2×10^{14}	442	1.3
Ar	27	1.45×10^{15}	442	2.5
Ar	27	4.34×10^{15}	442	7.5
Ar	27	8.69×10^{15}	442 <td 14.7	
Xe	70	0	1331	0
Xe	70	5×10^{14}	1331	2.7
Xe	70	1×10^{15}	1331	5.3
Xe	70	2×10^{15}	1331	10.5
Xe	70	3×10^{15}	1331	15.7

pressed, beneficial for thermoelectric materials²². Recent studies have investigated the effects of ion implantation of S, Se, and Te as dopants in CuI, but the effect of the implantation damage itself remained unclear^{23–25}. Implanting noble gas ions into a material is an excellent testing ground by which to investigate the properties of intrinsic point defects therein. Additionally, it is a process which can be applied without the need for high temperature processing, which generally causes a loss in electrical conductivity of CuI^{26–30}.

Noble gas ions provide the opportunity to modify the structure of thin films without also performing chemical modification, allowing the effects to be studied independently. In this work we implanted Ne, Ar, or Xe ions to modify the electronic properties of conducting transparent CuI thin films by introducing point defects. Overall, this process results in an enhanced p -type conductivity in CuI. This was identified to be due to an increased Hall carrier concentration with only a minor reduction in Hall carrier mobility. Further investigation on its thermoelectric properties suggest a variation of the scattering process toward ionized impurity scattering. The fast and ambient temperature implementation of this modification process makes it a low cost step during the device fabrication process.

A previous publication outlines the 60 – 70 nm CuI film deposition by ion beam sputtering process³¹. The CuI films were implanted with neon, argon, or xenon, at 13 keV, 27 keV, or 70 keV, respectively, to provide equivalent projected ranges (26 nm), with the implantation fluences scaled to approximately match the displacements per atom (DPA) calculated with the software Stopping Range of Ions in Matter (SRIM) in the *Detailed Calculation with full Damage Cascades* mode³². Due to the strong texture of the CuI films, the implantation was conducted at 7° from the sample normal. The relationship between implantation fluence (F), the displacements per ion (D), the atomic density ($\rho_n = 3.385 \times 10^{22}$ at cm⁻³),

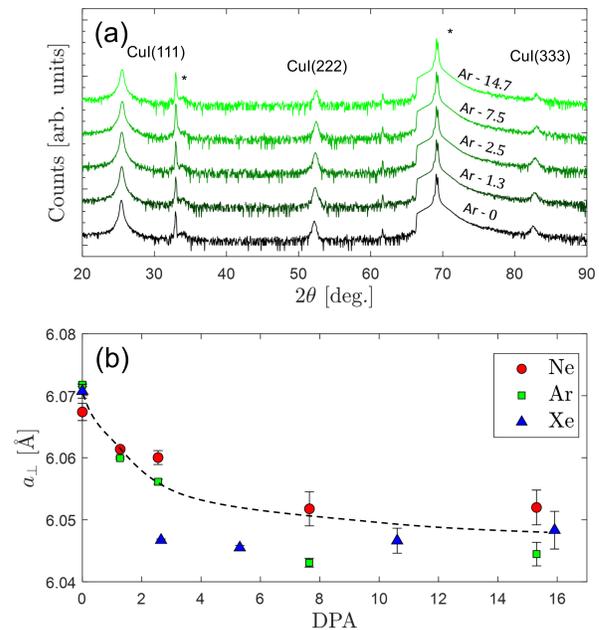


FIG. 1. (a) Angle-symmetric X-ray diffractograms, vertically offset for visual clarity. (b) Out-of-plane lattice constants derived from the XRD measurement, the dashed line is used as a guide.

and the resultant DPA (averaged over the 70 nm initial film thickness) are written as $DPA = FD/\rho_n$, and summarized in Table I. The samples were not visibly affected by implantation. Throughout this work the samples are labelled by the implantation species with the associated DPA (see Table S1 for a summary of sample details). The implantation and DPA depth profiles are included as Figures S1(a-f). More details pertaining to the implantation method are covered in previous publications^{24,25}.

The films' composition and thicknesses were investigated with Rutherford backscattering spectrometry (RBS). The RBS measurements were conducted with a 2.0 MeV ⁴He⁺ beam with a 165° backscattering angle, a current density of 10 nA and an integrated charge of 20 μC with a surface barrier detector³³. The backscattering spectra are shown in Figures S2(a-c), which suggest that the as-deposited films possessed stoichiometric [Cu]/[I] ratios of 1.02 ± 0.02 . The implanted samples exhibited increasing [Cu]/[I] ratios to an average of 1.16 ± 0.07 when implanted to an average DPA of 15, the ratios of which are included in Figure S3. Excess copper in CuI is commonly observed for thin films^{29,30,34,35}. The loss of iodine, and excess of copper is a result of preferential halide sputtering, subsequently oxidising the film surface upon exposure to air^{36–38}.

The films' structural properties were studied with X-ray diffraction using a Rigaku SmartLabs diffractometer, employing a Cu X-ray source. The angle-symmetric measurements are shown for the argon implanted samples in Figure 1a and Figures S4(a-b) for the others, resulting

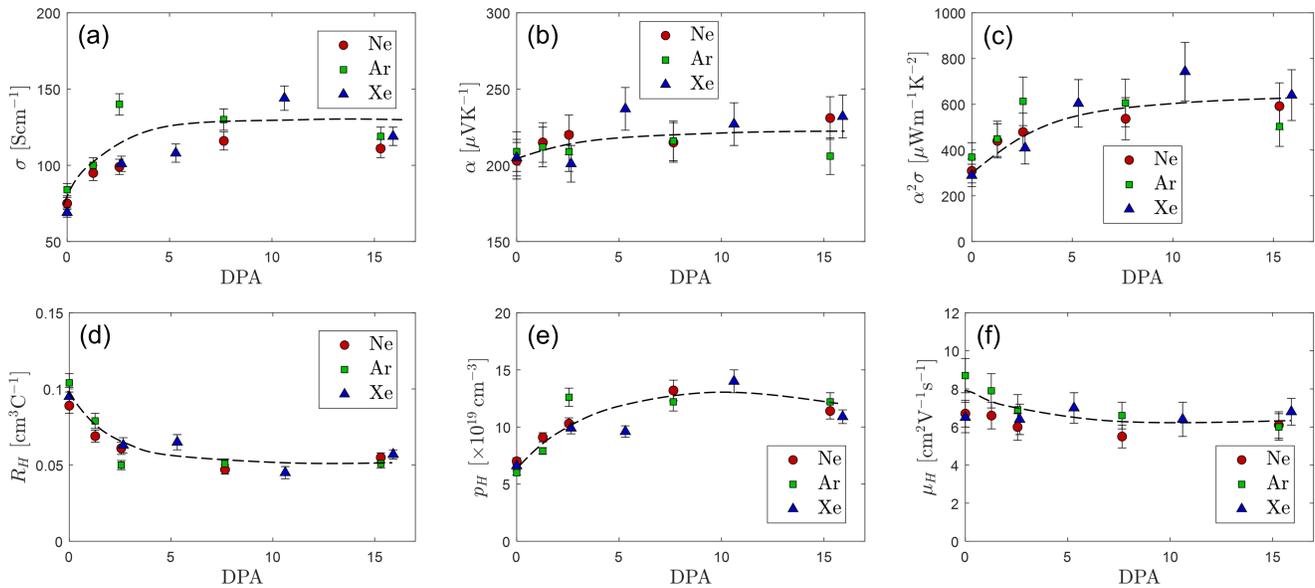


FIG. 2. (a) Electrical conductivity, (b) Seebeck coefficient, (c) Hall coefficient, (d) power factor, (e) Hall carrier concentration, and (f) Hall carrier mobility of CuI films implanted with noble gas ions. The dashed lines are used as a guide.

in the identification of the zincblende CuI, strongly textured along the $\langle 111 \rangle$ direction¹⁰. The lattice constants of the as-deposited films are $6.070 \pm 0.002 \text{ \AA}$, settling to $6.048 \pm 0.004 \text{ \AA}$ when implanted to an average DPA of 15, calculated using the goniometer error function³⁰. These are shown in Figure 1b, and the fits themselves depicted in Figures S5(a-c). The out-of-plane lattice constant of CuI thin films are well known to be greater than the bulk value of 6.054 \AA , but is known to not be strongly dependant on the $[\text{Cu}]/[\text{I}]$ ratio^{10,30}. CuI thin films grown along the (111) plane is known to be trigonally distorted, associated with a contraction (an expansion) of the out-of-plane (in-plane) lattice constants³⁹.

To evaluate the thermoelectric and carrier properties of the CuI thin films, the Seebeck coefficient α , electrical conductivity σ , and Hall coefficient R_H were measured. Room temperature Seebeck coefficient measurements were conducted with an ADVANCE RIKO ULVAC ZEM-3 with pressed nickel contacts. Hall effect measurements were conducted with an HMS-3000 after sputtering gold contacts on the corners of the samples. The systematic measurement errors for the Seebeck effect measurements are 6% due to systematic uncertainties^{41,42}, and 5% for and Hall effect measurements. The results of those measurements are summarized in Figure 2(a-f). The Seebeck and Hall coefficients were positive for all samples. The electrical conductivity increased from $76 \pm 2 \text{ Scm}^{-1}$ to $116 \pm 3 \text{ Scm}^{-1}$ for the unimplanted, and samples with highest DPA, respectively, an increase of $53 \pm 6\%$. The Seebeck coefficient slightly increased between the unimplanted samples ($206 \pm 7 \text{ \muVK}^{-1}$) and the samples with highest DPA ($223 \pm 8 \text{ \muVK}^{-1}$). The increasing electrical conductivity results in the improvement of the power factor, calculated from $\alpha^2\sigma$, the values ranging

from $322 \pm 32 \text{ \muWm}^{-1}\text{K}^{-2}$ to $578 \pm 58 \text{ \muWm}^{-1}\text{K}^{-2}$. Overall, the highest power factor was observed for the Xe-10.5 sample with a power factor of $743 \pm 128 \text{ \muWm}^{-1}\text{K}^{-2}$. This result exceeds the highest CuI thin film power factors of Coroa *et al.*¹⁵ ($467 \text{ \muWm}^{-1}\text{K}^{-2}$), Bae *et al.*³⁵ ($681 \text{ \muWm}^{-1}\text{K}^{-2}$), and Mirza *et al.*⁴⁰ ($481 \text{ \muWm}^{-1}\text{K}^{-2}$), but lower than those of Almasoudi *et al.*²⁸ ($1632 \text{ \muWm}^{-1}\text{K}^{-2}$). Concomitant with the increase in electrical conductivity, there was a reduction in the average Hall coefficient from $0.096 \pm 0.010 \text{ cm}^3\text{C}^{-1}$ to $0.054 \pm 0.005 \text{ cm}^3\text{C}^{-1}$. The Hall coefficient is related to the carrier concentration in the single parabolic band model by $p = (qR_H)^{-1}$, wherein q is the elementary charge. The derived Hall carrier concentrations increase from an average of $6.5 \times 10^{19} \pm 0.1 \times 10^{19} \text{ cm}^{-3}$ to an average of $11.5 \times 10^{19} \pm 0.4 \times 10^{19} \text{ cm}^{-3}$, an increase of $77 \pm 4\%$. Also, the Hall carrier mobility can be derived from $\mu_H = R_H\sigma$, reducing slightly from an initial value of $7.3 \pm 0.5 \text{ cm}^2 \text{ V}^{-1}\text{s}^{-1}$ to $6.3 \pm 0.4 \text{ cm}^2 \text{ V}^{-1}\text{s}^{-1}$. Such an effect, where the electrical conductivity increases by ion irradiation with a $-16 \pm 14\%$ reduction in Hall mobility has before been noted in Bi_2Te_3 which resulted in an improved thermoelectric power²⁰. It is possible that the point neutral and ionized disorder introduced by implantation is the cause for the reduction in carrier mobility. Willis *et al.*⁹ summarize the state-of-the-art results to which the results of this work can be directly compared.

The combined variation in Hall carrier concentration, Seebeck coefficient, and Hall carrier suggest that there is a change in the carrier scattering process. To further investigate this, the semiclassical Boltzmann transport model in the relaxation time approximation is applied³¹. To investigate variations in scattering mechanism the Seebeck coefficient is plotted against the Hall carrier con-

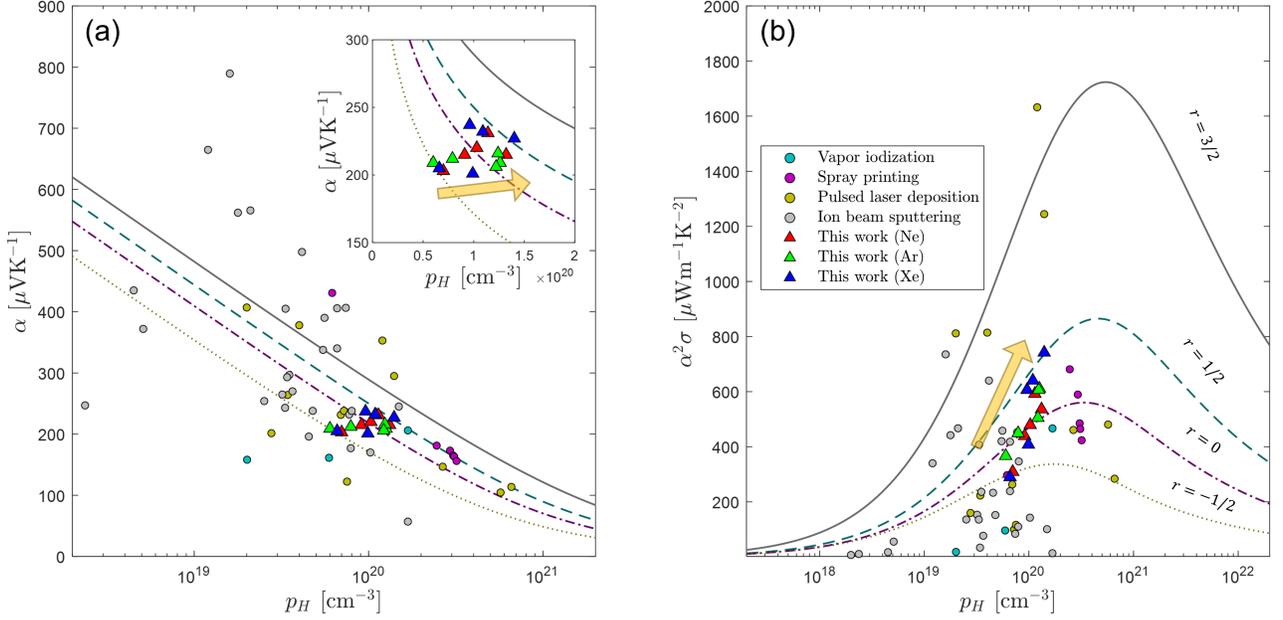


FIG. 3. (a) Seebeck coefficient and Hall carrier concentration plot with the corresponding Boltzmann transport equation solutions by using various scattering mechanisms (r). A survey of original literature data^{15,28,35,40} (colored circles) compared to previous^{23–25,27} is compared to the experimental findings of neon (red, squares), argon (green, diamonds), and xenon (blue, triangles). Inset graph presents a magnified view of the observed Hall carrier concentration and Seebeck coefficients. (b) Power factor plotted against Hall carrier concentration for the same data from literature. Arrows are used to imply the progression of the thermoelectric material properties with increasing DPA.

centration in Figure 3a, in addition to the corresponding theoretical curves. The results are also compared to results from CuI thin films in literature^{15,23–25,27,28,35,40}. The inset Figure 3a presents a magnified view of the results, which suggest a deviation from the conventional relationship of decreasing α with increasing p . This can be attributed to a change from deformation potential scattering toward ionized impurity scattering, as expected due to the increased Hall carrier concentration. The power factor is compared to the Hall carrier concentration and the corresponding Boltzmann transport equations in Figure 3b (by using $\tau_0 = 6.5$ fs). The scattering process is implied to change as the data does not track along any particular r curve. The highest-performing samples across literature possess Hall carrier concentrations of the order of $10^{20} - 10^{21} \text{ cm}^{-3}$.

The cause for the increased carrier concentration is presumably due to the increased concentration of copper vacancies, or alternatively, an increased concentration of interstitial iodine, although those possess a greater formation energy⁴³. Darnige *et al.*²⁹ hypothesized that during thin film growth, a large concentration of Frenkel pairs (complexes of vacancies and interstitials of the same type) are included which can be annealed out, resulting in a reduced carrier concentration after annealing^{26–28}. In addition to those produced during growth, Frenkel pairs are produced in abundance through ion implantation, es-

pecially in ionic crystals, which could be the reason for the increased carrier concentration³⁶. A connection between Frenkel pairs and the macroscopic electrical properties can be made by use of density functional theory (DFT) calculations, such as was done for $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ ⁴⁴, CeO_2 ⁴⁵, ThO_2 ⁴⁶, and $\text{CsPb}(\text{I}_{1-x}\text{Br}_x)_3$ ⁴⁷.

We conduct density functional theory calculations for intrinsic defects in CuI, such as vacancies ($V_{\text{Cu}}/V_{\text{I}}$), antisites ($\text{Cu}_{\text{I}}/\text{I}_{\text{Cu}}$), and interstitials ($\text{Cu}_{\text{i, tet-I}}/\text{I}_{\text{i, tet-I}}/\text{Cu}_{\text{i, tet-Cu}}/\text{I}_{\text{i, tet-Cu}}$), using the same computational setup using the PBE exchange-correlation functional as discussed in our previous work^{24,25}. The interstitial sites are coordinated tetragonally either by Cu ions, or I ions⁴⁸. The calculated formation and thermodynamic transition energies are in good agreement with the work of Huang *et al.*⁴³, for both the Cu-rich and Cu-poor chemical potential limits. Taking a step further, the Frenkel pair binding energy is calculated with

$$E_{b,D_1:D_2}^q = \Delta H_{D_1}^q + \Delta H_{D_2}^q - \Delta H_{D_1:D_2}^q \quad (1)$$

which relates the formation energy of the isolated defects ($\Delta H_{D_1}^q$ and $\Delta H_{D_2}^q$) with the formation energy of the defect complex ($\Delta H_{D_1:D_2}^q$)^{44,49}. A positive binding energy ($E_{D_1:D_2}^q$) indicates that the defects are stable complexes and will remain in proximity of one another, but, it does not indicate the likelihood of the formation thereof, which

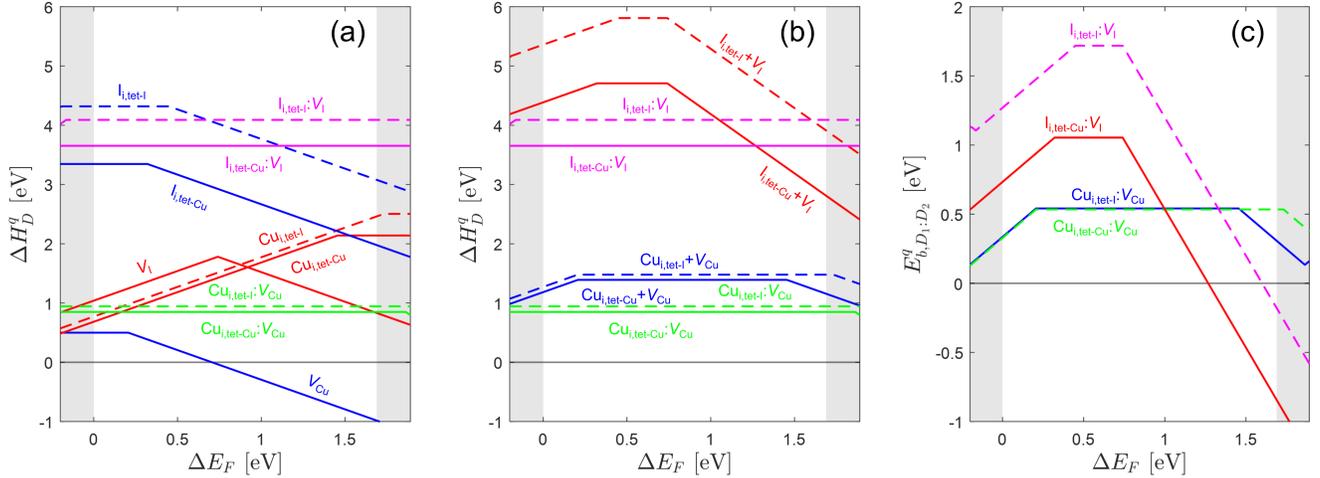


FIG. 4. (a) Formation energy of isolated and Frenkel defects. (b) Summed formation energies of the relevant isolated defects compared to their defect complexes. (c) Frenkel pair binding energy diagram. The defects involving the interstitial atoms coordinated by iodine (copper) atoms are drawn as dashed (filled) lines.

relies on a low formation energy of the defect complex ($\Delta H_{D_1;D_2}^q$). Figure 4a shows the formation energy of the isolated defects and defect complexes in CuI, Figure 4b shows the summed isolated defect formation energies, while Figure 4c shows the Frenkel pair defect binding energies calculated using Eq. 1.

Due to the low formation energy of V_{Cu} the self-consistently calculated Fermi energy is always near the valence band edge⁴⁸. When the Fermi energy is near the valence band edge, the pair of isolated defects (V_{Cu} and $Cu_{i,tet-I}/Cu_{i,tet-Cu}$) overall exhibit donor status. On the other hand, the charge of the Frenkel pairs remains neutral, which acts to passivate the compensating donors. Such a phenomenon has been previously used to describe the relation to macroscopic conductivity-switching effect based on different charge states of the isolated defects and their Frenkel pair binding energies in $Cd_{1-x}Zn_xTe$ ⁴⁴. Additionally, the effect of hydrogen passivation of cation vacancies in $CuMO_2$ ($M=Al, Ga, In$) was similarly investigated⁴⁹. This donor passivation effect is exacerbated by ion implantation, where Frenkel pairs are produced in abundance within the CuI matrix, leading to an overall p -type doping effect.

In summary, noble gas ion implantation with Ne, Ar, or Xe is a post-deposition technique to modify the transparent conducting and thermoelectric properties of CuI thin films by introducing intrinsic point defects. The out-of-plane lattice constant reduced from the as-deposited values of $6.070 \pm 0.002 \text{ \AA}$ to $6.048 \pm 0.004 \text{ \AA}$ for the highest-implanted films. Simultaneously, there was a remarkable improvement in electrical conductivity from an average of $76 \pm 2 \text{ Scm}^{-1}$ to $116 \pm 3 \text{ Scm}^{-1}$ by implantation to an average DPA of 15, regardless of the noble gas ion. This was mainly attributed to the increase in Hall carrier concentration, which increased from $6.5 \times 10^{19} \pm 0.1 \times 10^{19} \text{ cm}^{-3}$ to $11.5 \times 10^{19} \pm 0.4 \times 10^{19} \text{ cm}^{-3}$. The increasing Hall car-

rier concentration could be due to (1) the damage profile caused by the implantation resulting in the formation of Frenkel pairs which suppress the concentration of compensating donors, or (2) the replenishment of O into V_I near the film surface. It should be noted that O is known to not be a very shallow acceptor within CuI, and is not expected to drive the carrier concentrations above 10^{20} cm^{-3} .

The power factor of CuI thin films increased from an average of $322 \pm 32 \mu\text{Wm}^{-1}\text{K}^{-2}$ to $578 \pm 58 \mu\text{Wm}^{-1}\text{K}^{-2}$ by ion implantation with noble gas ions, comparable to the state-of-the-art power factors reported in literature. This improvement in the thermoelectric properties is likely due to a change in scattering mechanism from phonon to ionized impurity scattering, achieved by ambient temperature defect engineering with ion implantation.

CREDIT AUTHORSHIP CONTRIBUTION STATEMENT

MM: conceptualization, data curation, formal analysis, investigation, methodology, software, visualization, writing – original draft and editing. **PPM:** funding acquisition, supervision, validation, writing – review. **TM:** funding acquisition, writing – review. **JVK:** funding acquisition, supervision, validation, writing – review. **BJR:** funding acquisition, supervision, validation, writing – review.

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