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Energy landscape in silver-bismuth-iodide rudorffites: Combining scanning tunneling spectroscopy and Kelvin probe force microscopy

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We report energy-landscape of an upcoming solar cell material series, namely silver-bismuth-iodide rudorffites ($A_mB_nX_{m+3n}$). We have formed the compounds through compositional engineering and characterized them. We have employed Kelvin probe force microscopy (KPFM) to derive surface work-function and thereby Fermi energy; scanning tunneling spectroscopy (STS), on the other hand, provided conduction and valence band-edges with respect to Fermi energy of the rudorffites. By combining KPFM and STS studies, we have obtained a composition-dependent tuning of Fermi energy in the rudorffite thin-films, namely Ag_3BiI_6 , Ag_2BiI_5 , $AgBiI_4$, $AgBi_2I_7$, and $AgBi_3I_{10}$ with a gradual change in electronic conductivity from a p -type to an n -type. While such a behavior has been correlated to point-defects, which are possible to form in the different members of the rudorffite series, we more importantly show that a combination of KPFM and STS studies can provide a complete energy landscape in a semiconductor.

Keywords: Rudorffites; energy levels; shift in Fermi energy; scanning tunneling spectroscopy; Kelvin probe force microscopy.

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I. INTRODUCTION

The emergence of perovskite solar cells is considered to be one of the most significant achievements in photovoltaic research [1-3]. The success of methylammonium lead iodide ($\text{CH}_3\text{NH}_3\text{PbI}_3$) and its derivatives has provided additional impetus to researchers towards a search for compounds beyond the wonder material with nontoxic elements [4,5]. In this direction, compounds belonging to the rudorffite family with a generic formula of $A_mB_nX_{m+3n}$ have attracted a large interest due to their superior optoelectronic properties as compared to other lead-free perovskites in terms of a higher structural dimensionality, a favorable band gap, high absorption coefficients, low exciton binding energies, superior carrier transport properties, and environmental stability [6-14]. In the generic formula, A and B represent a monovalent and a trivalent element, respectively; while X corresponds to a halogen, m and n are integers. The solar-to-electricity power conversion efficiencies (PCE) in devices based on these compounds, which were first synthesized in 2016, have so far reached to 5 %. These results are quite promising and have implied significant scope for further improvement through (1) device-structure optimization and (2) materials-engineering, although the two processes are quite interlinked [7,9].

The process of device-structure optimization involved formation of regular ($n-i-p$) or inverted ($p-i-n$) heterojunctions followed by selection of suitable hole- and electron-transport materials, so that a type-II band-alignment is formed at both the interfaces [15-18]. A suitable band-aligned heterojunction is also a well-established key to suppress recombination of carriers at the defect-sites of rudorffites to achieve PCEs towards their radiative limit [19-21]. In regard to materials-engineering, the integers in $A_mB_nX_{m+3n}$ are varied in forming a series of compounds based on a set of elements. Amongst the rudorffites, the common series has so far been the one based on silver, bismuth, and iodine as the building-block elements; a variation in m and n has led to formation of a series of compounds which were considered in fabricating solar cells with suitable carrier-transporting materials [6-14]. Interestingly, optical band gap of compounds in the $A_mB_nX_{m+3n}$ series could be found to remain unaltered with a variation in m and n , while the device performance diverged widely presumably due to a change in the nature of band-alignments with carrier-transport layers.

It can hence be envisaged that conduction and valence band (CB and VB, respectively) edges of the compounds and/or Fermi energy (E_F) may depend on the composition of the rudorffites, that is m and n in the $A_mB_nX_{m+3n}$ series while retaining their band gap. In this direction, we have combined scanning tunneling spectroscopy (STS) and Kelvin probe force microscopy (KPFM) in estimating the band-edges and E_F of the compounds with respect to vacuum level. Such measurements will be somewhat superior over optical spectroscopy, cyclic voltammetry (CV), and ultraviolet photoelectron spectroscopy (UPS) [16,17,22] while visualizing the band-alignment at the interfaces and drawing a band-diagram of heterojunction devices with energies as actually encountered by charge carriers [17,23].

In this work, we first of all employed KPFM in determining surface work function (W_F); while evaluating W_F ($-E_F$), KPFM has an advantage over photoemission spectroscopy (PES), since the latter mode of measurement may have an influence due to additional surface photovoltage appearing upon illumination and also a light-induced band-bending process [24]. The absolute E_F in the rudorffite compounds can be probed as an equal and opposite of the W_F if surface effects are neglected. Hereafter, the CB and VB-edges were determined with respect to E_F in STS studies, although a shift in the band-edges may occur due to a tip-induced-band-bending (TIBB) in semiconductors that are not significantly doped [25]. Here, through combined KPFM and STS studies, we have drawn energy landscape of the rudorffite series and correlated the results with point-defects expected to exist in different members of the series.

II. MATERIALS AND METHODS

A. Materials

Silver iodide (AgI, 99 %), bismuth iodide (BiI_3 , 99 %), anhydrous N,N-dimethyl formamide (DMF, 99.8 %), dimethyl sulfoxide (DMSO), and 1,2-dichlorobenzene (DCB, anhydrous 99 %) were purchased from Sigma-Aldrich Chemical Company. All the materials were kept inside a nitrogen-filled glovebox with well-maintained oxygen and moisture levels below 0.1 ppm and used without further purification.

B. Formation of the thin-films

Thin-films of the rudorffite compounds were formed from their precursors, namely AgI and BiI_3 in required proportions in a mixture of DMF and DMSO (1:4, v/v) following the work of Miyasaka and his group [10]. The solutions were kept at 70 °C under a continuous stirring condition until the precursors dissolved properly in forming a clear and homogeneous solution. The substrates for film-deposition, namely quartz, indium tin oxide (ITO) coated glass, and *n*-type (arsenic doped) polished silicon were cleaned following a usual protocol followed by an UV-ozone treatment to remove organic residues. The substrates were then transferred to the glovebox; precursor solutions were spun separately on the substrates at 4000 rpm for 60 s followed by an antisolvent treatment of DCB during the last 10 s. The films were then dried in vacuum of the antechamber for a partial evaporation of solvent, followed by a two-step thermal annealing at 110 °C for 15 min and 160 °C for 15 min in sequence.

C. Characterization of the thin-films

Optical and structural characterization of the thin-films were performed through UV-visible optical absorption spectroscopy and X-ray diffraction studies using a Shimadzu UV-2550

spectrophotometer and a Bruker-D8 X-ray diffractometer (Cu $K\alpha$ radiation, $\lambda = 1.54 \text{ \AA}$), respectively. Kelvin probe force microscopy (KPFM) was carried out in a Nanosurf C3000 atomic force microscope with a Cr/Pt coated Si tip (Multi 75EG); for this purpose, the rudorffite films were formed on ITO substrates. The work function of the tip was calibrated to $4.77 \pm 0.02 \text{ eV}$ when measured with respect to a standard sample, namely highly oriented pyrolytic graphite (HOPG, $W_F = 4.65 \text{ eV}$). Scanning tunneling microscopy/spectroscopy (STM/S) was performed in a Nanosurf Easyscan2 scanning tunneling microscope. For such measurements, ultrathin-films were cast on the silicon substrates from a one-order dilute precursor solutions. The STM tips were formed through a mechanical cut of a Pt-Ir (80:20) wire having a diameter of 0.25 mm. The tip was brought into the tunneling region using a feedback loop; the tip-approach condition was 1.0 nA at 2.0 V. To record STS, the feedback loop was disabled to maintain a fixed tip-to-sample separation. Tunneling current versus voltage characteristics were recorded by swiping the tip voltage in the $\pm 2.0 \text{ V}$ range. The derived dI/dV spectra had a direct correspondence to the DOS of the samples (*vide infra*).

II. RESULTS AND DISCUSSION

A. Characterization of rudorffite thin-films

In this work, we have considered thermodynamically-stable Ag_3BiI_6 , Ag_2BiI_5 , AgBiI_4 , AgBi_2I_7 , and $\text{AgBi}_3\text{I}_{10}$ rudorffites in the $A_mB_nX_{m+3n}$ series in determining their band-edges and electronic conductivity. As mentioned earlier, thin-films of the compounds were formed from their precursors, namely AgI and BiI₃ in required proportions following the work of Miyasaka and his group [10]. The films were characterized through optical absorption spectroscopy and X-ray diffraction (XRD) patterns in order to ensure phase-purity of the compounds. In Fig. 1(a), optical absorption spectra of different $A_mB_nX_{m+3n}$ compounds in their thin-film forms have been presented. Tail states were additionally observed due to the scattering of light by rough film morphologies. Similar to conventional hybrid halide perovskites, rudorffites have exhibited a high absorbance over the entire spectral range; the spectra matched well with the reported results [7-11,14]. Optical band gap of the materials could be estimated from Tauc plots (Fig. 1b). In all the compounds, the gap was found to be identical ($\sim 1.80 \pm 0.05 \text{ eV}$), which matched closely to the literature, inferring that the band gaps of the rudorffite compounds were invariant with the composition [7-11,14]. Considering the difficulty of using Elliott formula [26] in calculating the optical bandgap more accurately when Tauc plots may not fit well, we have presented the $\frac{d(\alpha \hbar\nu)^2}{d(\hbar\nu)}$ versus $\hbar\nu$ plots as an alternative to determine the bandgap Fig. 1c). The results show that the optical bandgap did not diverge upon a variation in the composition; the bandgap ranged within a small window of 1.93 – 2.02 eV.

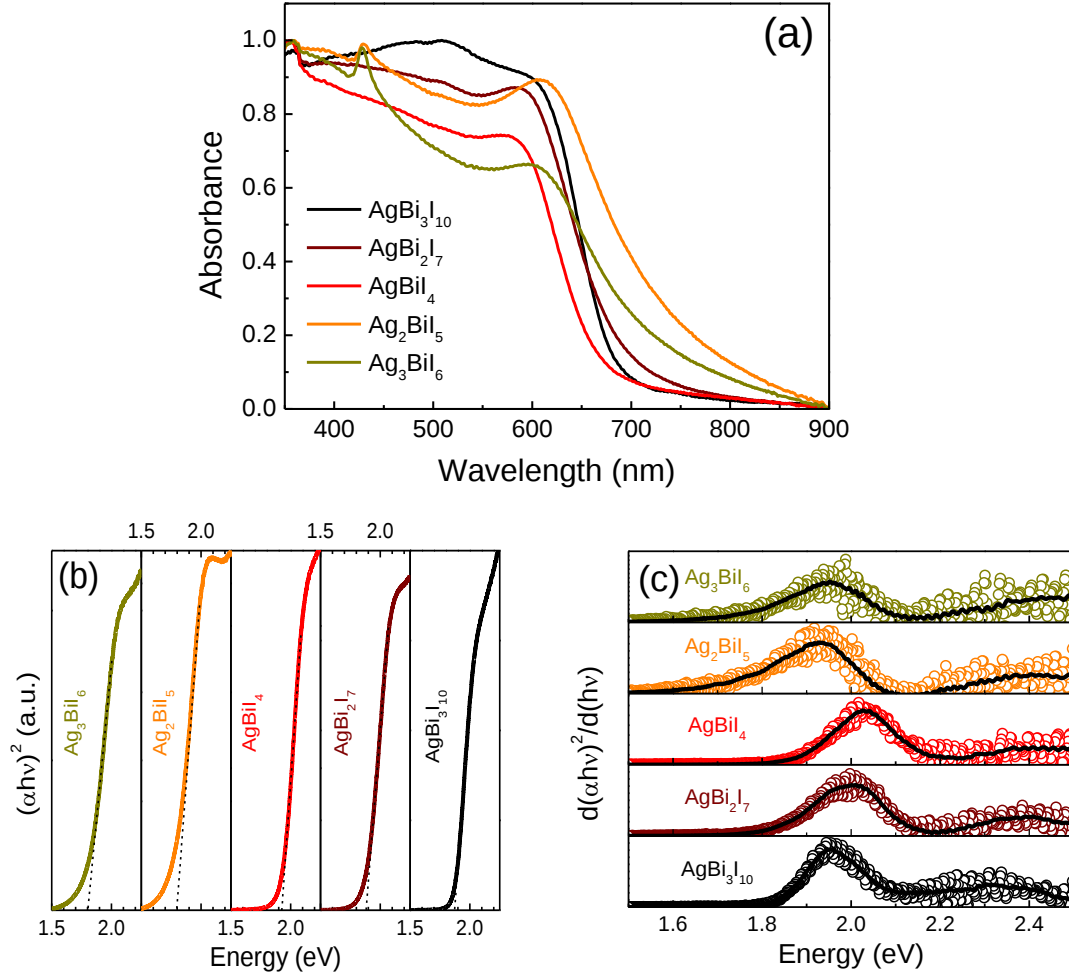


FIG. 1. (a) Optical absorption spectra, (b) Tauc plots, and (c) $\frac{d(\alpha h\nu)^2}{d(h\nu)}$ versus $h\nu$ plots of $A_mB_nX_{m+3n}$ thin-films. Composition of the compounds are shown in legends.

Due to a strong absorbance of the rudorffites in the visible region, optical spectroscopy is often considered inadequate to establish phase-purity of the compounds. Hence, we have recorded their XRD patterns (Fig. 2). The patterns of silver-rich rudorffites (Ag_2BiI_5 and Ag_3BiI_6) exhibited a highly crystalline rhombohedral phase with R-3m symmetry [7,9,14,27,28]. A trace amount of unreacted AgI bearing a hexagonal phase could be observed in these compounds [9]. On the other end, bismuth-rich rudorffites, namely AgBiI_4 , AgBi_2I_7 , and $\text{AgBi}_3\text{I}_{10}$ possessed a cubic crystal structure with a Fd-3m space group symmetry [6,8-11,27-31]. In AgBiI_4 thin-films, peaks arising from Ag_2BiI_5 having a rhombohedral phase were additionally observed [8]. In this regard, Sansom et al. have proposed that AgBiI_4 crystallizes in either R-3m or Fd-3m phase which are indistinguishable through XRD studies [31]. It may also be stated that the bismuth-rich rudorffites (AgBi_2I_7 and $\text{AgBi}_3\text{I}_{10}$) contained peaks from unreacted BiI_3 as

well that has a rhombohedral phase [9,10]. In Table I, we have presented experimentally-observed crystallographic data of different rudorffite compounds used to identify their crystal structures and phase-groups.

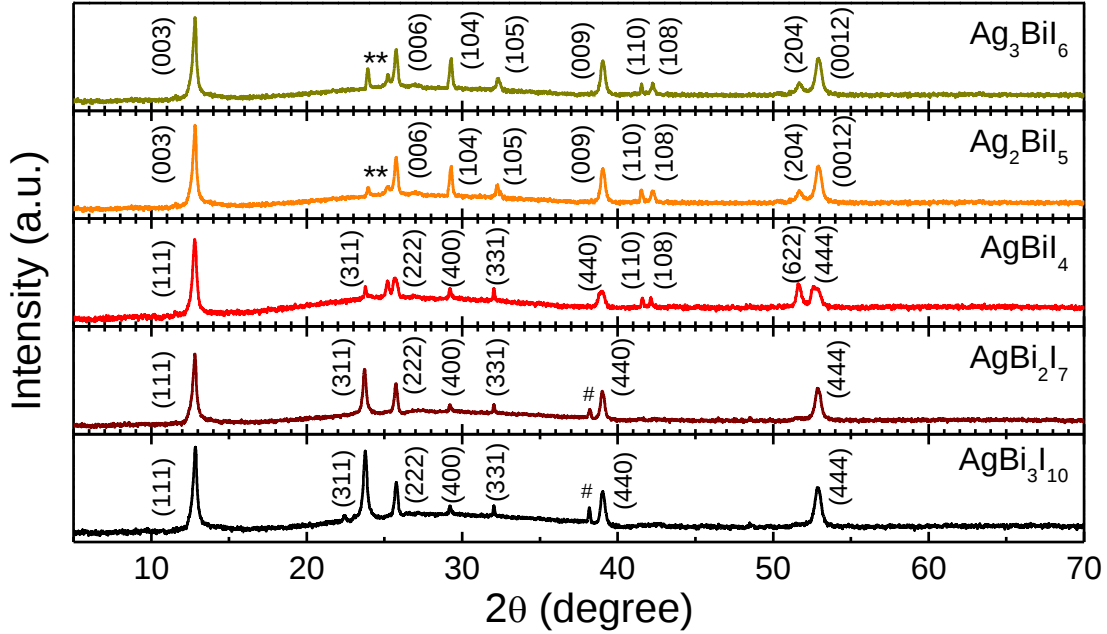


FIG. 2. XRD patterns of different $A_m B_n X_{m+3n}$ compounds. Intensity-axis has been presented in a logarithmic scale for better visualization of weak peaks as well. Patterns arising out of unreacted AgI and BiI₃ are marked with asterisk (*) and hash (#) symbols, respectively.

TABLE I. XRD peaks and crystallographic data of different $A_m B_n X_{m+3n}$ compounds in their thin-film form.

$A_m B_n X_{m+3n}$	Reflections (<i>hkl</i>)	2θ	Crystal Structure and Space Group	Impurity (angle)	References
Ag ₃ BiI ₆ (<i>m</i> = 3, <i>n</i> = 1)	(003)	12.8°	Rhombohedral (R-3m)	AgI (23.9°)	Oldag et al. [28]
	(006)	25.7°			
	(104)	29.1°			
Ag ₂ BiI ₅ (<i>m</i> = 2, <i>n</i> = 1)	(003)	12.9°	Rhombohedral (R-3m)	AgI (23.9°)	Mashadieva et al. [27]
	(006)	25.9°			
	(104)	29.2°			
AgBiI ₄ (<i>m</i> = 1, <i>n</i> = 1)	(111)	12.7°	Defect cubic spinel (Fd-3m) and rhombohedral (R-3m)	Ag ₂ BiI ₅ (41.5°, 42.2°)	Oldag et al. [28] Sansom et al. [31] Dzeranova et al. [29]
	(311)	24.2°			
	(222)	25.3°			
AgBi ₂ I ₇ (<i>m</i> = 1, <i>n</i> = 2)	(111)	12.6°	Defect cubic spinel (Fd-3m)	BiI ₃ (38.4°)	Fourcroy et al. [30] Mashadieva et al. [27]
	(311)	24.2°			
	(222)	25.3°			
AgBi ₃ I ₁₀ (<i>m</i> = 1, <i>n</i> = 3)	(111)	12.6°	Defect cubic spinel (Fd-3m)	BiI ₃ (38.4°)	Kim et al. [6]
	(311)	24.2°			
	(222)	25.3°			

B. Estimation of work function from Kelvin probe force microscopy

In order to determine the energy levels of the rudorffites, it is imperative to determine E_F of the compounds. As such, a direct analysis of E_F can be performed by studying surface work function (W_F) of the compounds [17,23,24,32]. In a semiconductor, the energy difference between E_F and vacuum level (E_{vac}) corresponds to W_F ; hence, a change in E_F is expected to result in an equal and opposite change in W_F if surface effects are neglected [24]. In this direction, we have carried out KPFM measurements in an amplitude-modulated single-pass mode where the cantilever passes over every line while simultaneously recording topography and contact potential difference (CPD) between the tip and the sample [33-34]. In order to obtain a better sensitivity and resolution in KPFM measurements, the amplitude of cantilever oscillation was kept small, so that the tip remains closer to the film surface. In principle, as the DC bias was applied to the tip, CPD between the sample and tip is defined as [34,35]:

$$CPD = W_F(Tip) - W_F(Sample) \quad (1)$$

where $W_F(Tip)$ and $W_F(Sample)$ are the work function of the Pt/Cr-coated tip and the sample, respectively. At first, the $W_F(Tip)$ was calibrated to 4.77 ± 0.02 eV when measured with respect to a standard sample, namely HOPG ($W_F = 4.65$ eV); the measured CPD values of the rudorffites were then converted to $W_F(rudorffite)$ as [34,35]:

$$W_F(rudorffite) = 4.77 - CPD(rudorffite) \quad (2)$$

In Fig. 3a, we have presented topographies (upper panel) and corresponding CPD maps (lower panel) of different $A_mB_nX_{m+3n}$ thin-films. After converting a CPD histogram (Fig. 3b) to $W_F(rudorffite)$, we observed that the $W_F(rudorffite)$ and hence $E_F (= -W_F)$ varied with the composition (Fig. 3c). The variation was as large as 0.5 eV when we scanned from silver-rich to bismuth-rich perovskites (from Ag_3BiI_6 to $AgBi_3I_{10}$). Full width at half maxima (FWHM) of the CPD-histograms was a measure of the disorders/defects in the materials that turned out to be higher for $AgBi_2I_7$, $AgBiI_4$, and Ag_2BiI_5 .

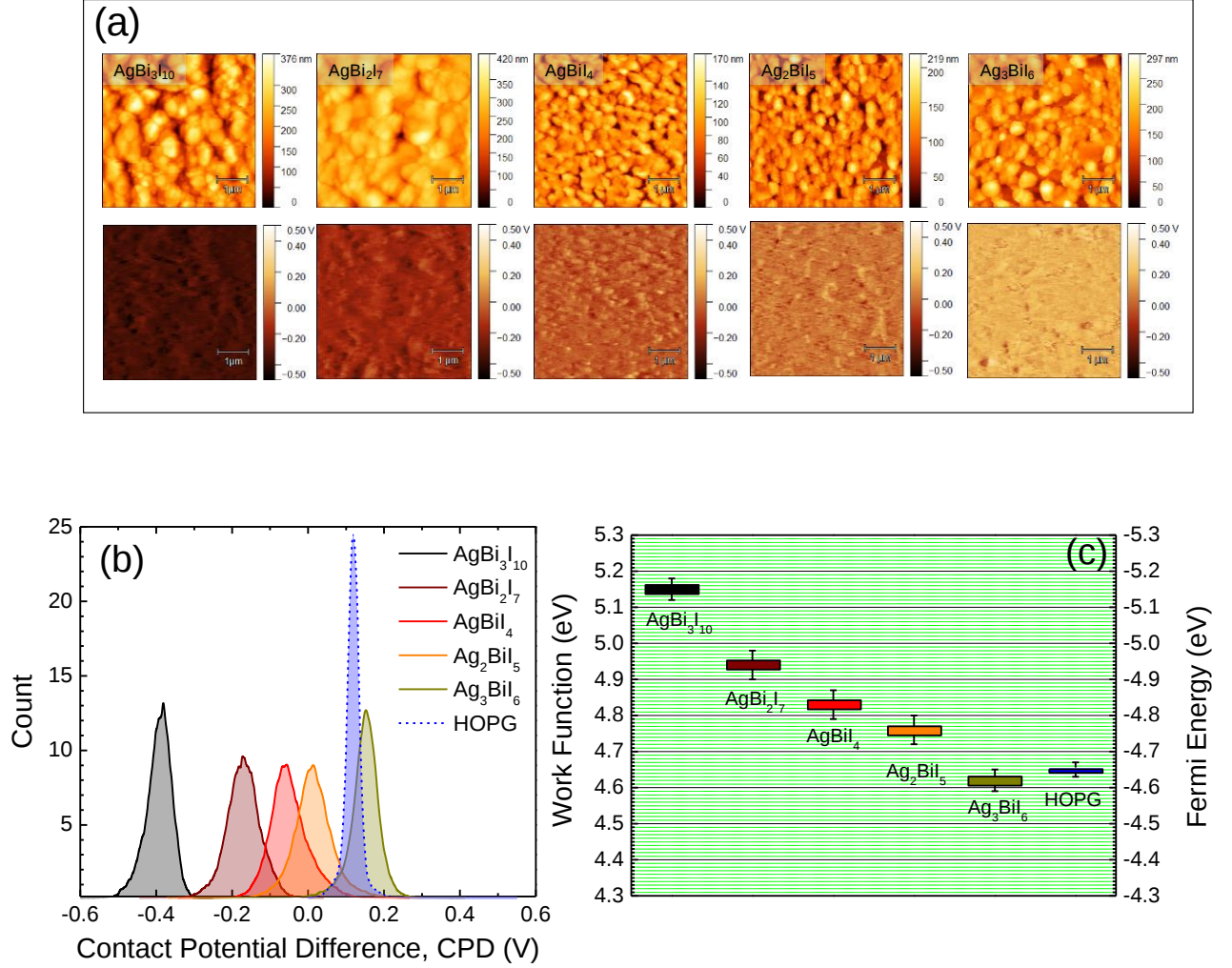


FIG. 3. (a) Topography (upper panel) and contact potential images (lower panel), (b) distribution of contact potential difference (CPD), and (c) average surface work function (W_F) and Fermi energy (E_F) from KPFM measurements of different $\text{A}_m\text{B}_n\text{X}_{m+3n}$ thin-films. Error-bars in (c) represent FWHM of the CPD-histograms.

C. Estimation of band-edges from scanning tunneling spectroscopy

Ensuring W_F and the energy of E_F , we have characterized the rudorffites in an STM to estimate their band edges with respect to E_F , so that a complete energy landscape of the materials can be achieved. Tunneling current was recorded and differential tunnel conductance (dI/dV) spectrum was derived in each of the compounds. In principle, STS provided dI/dV spectrum which has a correspondence to the density of states (DOS) of the semiconductor under study:

$$(dI/dV) \propto \text{DOS}_{\text{sample}}(E_F - E) \quad (3)$$

As bias was applied to the tip, the first peak in the positive voltage nearest to 0 V (E_F) of a dI/dV spectrum inferred withdrawal of electrons and hence the VB-edge of the semiconductor. In a similar manner, the first peak in the negative voltage closest to 0 V implied injection of electrons to an available energy level of the compound, that is, the CB-edge [17,23,32]. Accordingly, each dI/dV spectrum provided CB- and VB-edges with respect to E_F and thereby their nature of electronic conductivity. Since STS is an extremely localized mode of measurement, band-edges of the material at the exact point of tip-approach are obtained. Hence, tunneling current versus voltage characteristics were recorded at many different points on the surface of each rudorffite ultrathin-film. A set of VB- and CB-energies was obtained from each measurement; the results for a rudorffite compound were then collated to draw histogram of the band-energies. The histograms finally provided the band-energies of a compound with respect to E_F . Typical dI/dV spectra and histograms of different $A_mB_nX_{m+3n}$ compounds have been presented in Figs. 4a-b, respectively. As can be seen from the spectra, for a AgBiI_4 thin-film formed with balanced combination of AgI and BiI_3 , CB- and VB-edges appeared in the form of peaks at -0.84 ± 0.05 and 0.98 ± 0.05 eV, respectively, away from the E_F . In addition, the histograms in Fig. 4b infer that CB-energy in AgBiI_4 was slightly nearer to E_F than the VB-edge suggesting a quasi n -type electronic conductivity of the material. (Previously, AgBiI_4 , when synthesized in a powder form, was reported to possess a p -type nature with a low carrier-density [31]; the little deviation in the type of conductivity may have appeared due to a different synthesis route used in this work.) On the other hand, in silver-rich rudorffites (Ag_3BiI_6 and Ag_2BiI_5), while VB-edge moved towards E_F , the CB drifted away inferring a p -type conductivity in these materials; the upward shift of band-edges was somewhat counterbalanced by a shift of E_F towards the vacuum level and hence forbade yielding of a strong p -type character in these compounds. In bismuth-rich rudorffites, shift of the two bands was opposite as compared to those in silver-rich ones leading to an n -type conductivity in AgBi_2I_7 and $\text{AgBi}_3\text{I}_{10}$; the shift in band-edges in these compounds was again counterbalanced by the movement of E_F away from the vacuum level. In other words, the shift in band-edges was always partly compensated by a swing in E_F . This interesting observation may need further deliberation through studies in other similar series.

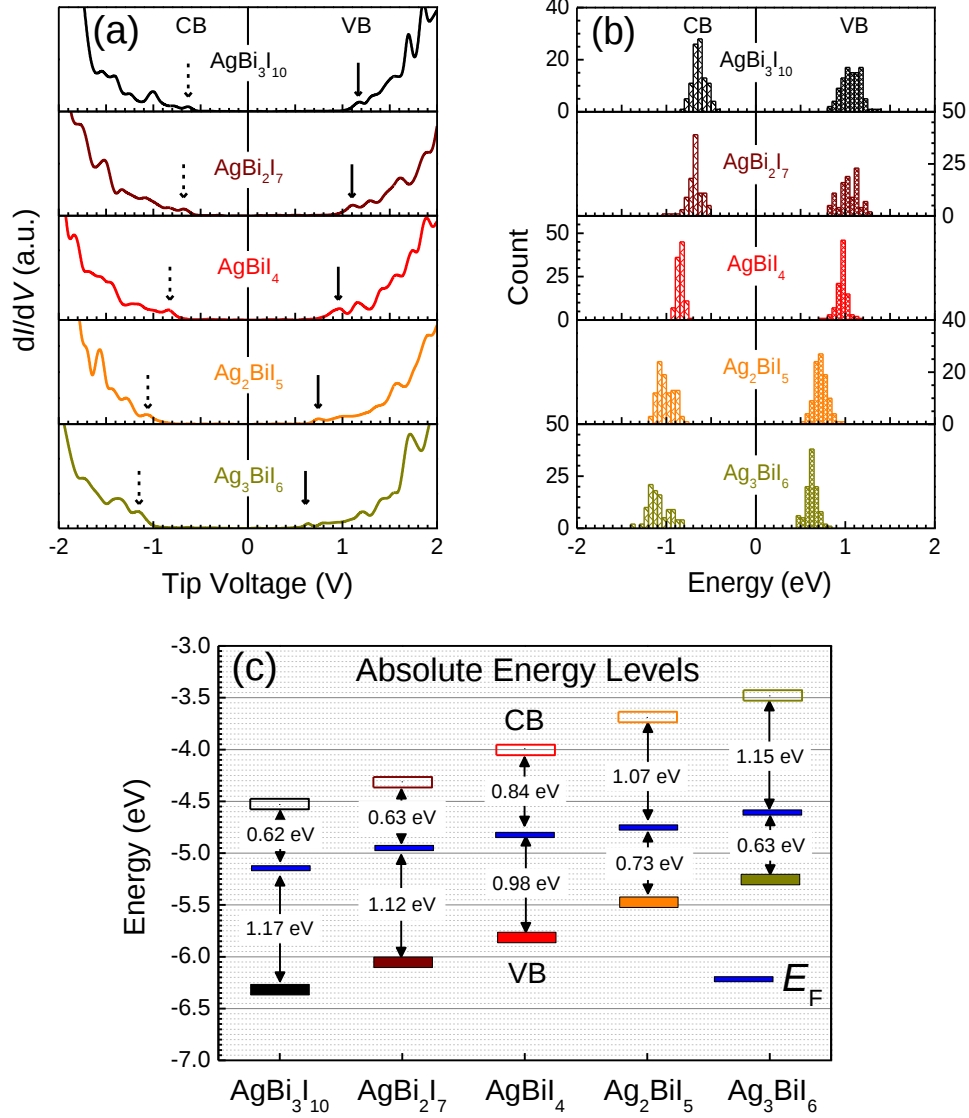


FIG. 4. (a) dI/dV versus tip voltage, (b) histogram of CB-and VB-energies, and (c) absolute band-edges with respect to vacuum ($E_{\text{vac}} = 0$ eV) from combined KPFM and STS studies of different $A_mB_nX_{m+3n}$ thin-films as stated in the legends.

In Fig. 4c, we have finally compiled the absolute band-energies of different rudorffite compounds as observed from combined KPFM and STS studies. In addition, the absolute energy levels, transport gap, and optical band gap of different rudorffites have been summed in Table II. Alike optical band gap, transport gap also remained invariant in the compounds. A small difference between the optical bandgap and the transport gap could be witnessed. Such a difference may arise from (1) involvement of exciton binding energy during optical absorption spectroscopy resulting in a smaller optical bandgap and/or (2) presence of defect-states during a tunneling process (STS) and consequent lowering of the transport gap.

As exciton binding energy is small in such compounds (~ 150 meV) as compared to organic molecules, which involve Frenkel excitons, contribution of midgap defect-states would be larger during the tunneling process resulting in a smaller transport gap [36]. The band-edges and E_F however varied strongly across the compounds. The individual band-energies that could be brought out from the measurements in effect allow one to view the nature of band-alignment at the p - i and i - n interfaces. The results hence bring out the importance of individual band-energies in designing both regular (n - i - p) and inverted (p - i - n) heterojunction solar cells based on different rudorffite thin-films and charge transport layers [17,23].

TABLE II. Band-energies with respect to E_F , absolute band-energies, transport gap, and optical band gap of different $A_mB_nX_{m+3n}$ thin-films.

Rudorffites	Fermi energy, E_F (eV)	Valence band, E_V (eV)		Conduction band, E_C (eV)		Transport gap (eV)	Optical band gap (eV)
		$E_F + E_V$	Absolute E_V	$E_F - E_C$	Absolute E_C		
Ag_3BiI_6	-4.63	0.63	-5.26	-1.15	-3.48	1.78	1.80
Ag_2BiI_5	-4.76	0.73	-5.49	-1.07	-3.69	1.80	1.81
AgBiI_4	-4.83	0.98	-5.81	-0.84	-3.99	1.82	1.90
AgBi_2I_7	-4.94	1.12	-6.06	-0.63	-4.31	1.75	1.88
$\text{AgBi}_3\text{I}_{10}$	-5.15	1.17	-6.32	-0.62	-4.53	1.79	1.87

D. Role of point-defects in the composition-dependent tuning of E_F

It may be seen that upon a change in the composition of the rudorffite, the E_F shifted monotonically. The results also infer a change in the type of conductivity (from p -type in Ag_3BiI_6 to n -type in $\text{AgBi}_3\text{I}_{10}$). Such a change might have caused a superior solar cell performances in Ag-rich rudorffites as compared to the Bi-rich ones [37] upon achieving a better band-alignment with charge transport layers. It is imperative to know the rationale for such a composition-induced shift in electronic conductivity in rudorffite thin-films. The shift can be correlated to the presence of point-defects generated during thin-film formations. Due to a lack of theoretical calculations, identification of point-defects in rudorffites remained challenging; that is, formation energy of different defects that may form in the materials is not known at the moment. However, based on the defect landscape of silver and/or bismuth halides, such as $\text{Cs}_2\text{AgBiBr}_6$ and $\text{Cs}_3\text{Bi}_2\text{I}_9$, we could propose possible point-defects that can tune the electronic conductivity of rudorffite thin-films from a p -type to an n -type as a function of composition [38-40]. We have observed that compounds formed with silver-rich precursors, such as Ag_3BiI_6 and Ag_2BiI_5 , exhibit p -type conductivity inferring involvement of acceptor-like point-defects. In Table III, we have proposed possible acceptor-like defects accountable for this nature. As such, we have observed that these compounds are formed with an unreacted AgI, although these compounds were formed with

stoichiometric precursors (AgI and BiI₃). Hence, formation of these compounds with silver-site vacancies (V_{Ag}) is quite plausible leading to their p -type nature. On the other hand, AgBiI₄ formed with stoichiometric AgI and BiI₃ showed a quasi n -type behavior. We presume that donor-type iodine vacancies (V_{I}) are primarily responsible to impose an n -type conductivity in the compound. Similarly, the bismuth-rich rudorffites, such as AgBi₂I₇ and AgBi₃I₁₀, demonstrated a stronger n -type nature signifying presence of more V_{I} in these compounds. In this regard, we have considered the role of residual BiI₃, which was present in these compounds, in facilitating donor-type V_{I} instead of V_{Bi} [41-43]. Secondary contributions of other donor-type point-defects cannot however be ruled out and have been appended in Table III. In view of this, this discussion might open further opportunities to investigate point-defects with least formation energies as a function of growth environment.

TABLE III. Possible point-defects present in $A_mB_nX_{m+3n}$ thin-films. The most probable defect-states are identified in bold.

$A_mB_nX_{m+3n}$ composition	Compounds	Conductivity	Acceptor-like defects (p -type)	Donor-like defects (n -type)
Silver-rich	Ag ₃ BiI ₆	p -type	(1) silver vacancies (V_{Ag}) (2) silver on bismuth substitution (Ag_{Bi}) (3) iodine on cation antisite substitution (I_{Bi}) (4) iodine interstitial (I_{i})	
	Ag ₂ BiI ₅	p -type		
Balanced	AgBiI ₄	quasi n -type	silver vacancies (V_{Ag})	iodine vacancies (V_{I})
Bismuth-rich	AgBi ₂ I ₇	n -type		(1) iodine vacancies (V_{I}) (2) bismuth on iodine substitution (Bi_{I}) (3) bismuth interstitial (Bi_{i})
	AgBi ₃ I ₁₀	n -type		

III. CONCLUSIONS

In conclusion, by combining STS and KPFM, we have estimated the electronic energy landscape of a series of rudorffite compounds, $A_mB_nX_{m+3n}$. Such information is important to form band-diagrams of heterojunctions for solar cell applications. Through a control over precursor-stoichiometry, Ag₃BiI₆, Ag₂BiI₅, AgBiI₄, AgBi₂I₇, and AgBi₃I₁₀ were formed and characterized; optical band gap of these compounds remained around 1.8 eV. KPFM measurements showed a linear shift in work-function and hence Fermi energy in these compounds. STS studies, on the other hand, evidenced a gradual shift in CB and VB-edges with respect to E_{F} and hence a change in electronic conductivity from a p -type to an n -type. The results (a change in the type of conductivity) have been correlated to point-defects existing in different members of the rudorffite series. We also show that a combination of KPFM and STS studies can provide a complete energy landscape in a semiconductor.

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AVAILABILITY OF DATA

The data that support the findings of this study are available from the corresponding author upon reasonable request.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

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