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Formation of a passivating $\text{CH}_3\text{NH}_3\text{PbI}_3/\text{PbI}_2$ interface during moderate heating of $\text{CH}_3\text{NH}_3\text{PbI}_3$ layers

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Layers of $\text{CH}_3\text{NH}_3\text{PbI}_3$ are investigated by modulated surface photovoltage spectroscopy (SPV) during heating in vacuum. As prepared $\text{CH}_3\text{NH}_3\text{PbI}_3$ layers behave as a p-type doped semiconductor in depletion with a band gap of 1.5 eV. After heating to 140 °C the sign of the SPV signals of $\text{CH}_3\text{NH}_3\text{PbI}_3$ changed concomitant with the appearance of a second band gap at 2.36 eV ascribed to PbI_2 , and SPV signals related to charge separation from defect states were reduced after moderate heating. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4826116>]

Rather high solar energy conversion efficiencies of almost 12 (Ref. 1) or 15% (Ref. 2) have been reached with solar cells based on $\text{CH}_3\text{NH}_3\text{PbI}_3$ absorber layers within a comparably short time of research and development. The band gap of $\text{CH}_3\text{NH}_3\text{PbI}_3$ layers is about 1.5 eV, and high open circuit voltages (V_{OC}) of 0.83 (Ref. 3) and 0.993 V (Ref. 2) have been measured on related solar cells by different groups. High values of V_{OC} of solar cells based on only 300–400 nm thin $\text{CH}_3\text{NH}_3\text{PbI}_3$ absorber layers² point to efficient surface passivation occurring during processing at low temperatures. This work is aimed to get more information about surface passivation of $\text{CH}_3\text{NH}_3\text{PbI}_3$ absorber layers during low temperature processing. For this purpose $\text{CH}_3\text{NH}_3\text{PbI}_3$ layers were heated in vacuum and investigated with the very sensitive method of modulated surface photovoltage spectroscopy (SPV).⁴

Layers of $\text{CH}_3\text{NH}_3\text{PbI}_3$ were prepared following a slightly modified procedure of Snaith.¹ First, $\text{CH}_3\text{NH}_3\text{I}$ has been produced by mixing methylamine and HI (sigma Aldrich). The resulting precipitate $\text{CH}_3\text{NH}_3\text{I}$ was washed three times using diethylether and re-crystallized in ethanol by adding ether (CH_3OCH_3). Second, PbI_2 was dissolved in γ -butyrolactone (sigma Aldrich), and $\text{CH}_3\text{NH}_3\text{I}$ was added in stoichiometric ratio. Third, the solution was stirred overnight at 60 °C. Fourth, layers of $\text{CH}_3\text{NH}_3\text{PbI}_3$ were deposited onto infrared pre-heated molybdenum coated soda lime glass substrates by spin coating (2000 rpm for 3 min) using a hot solution of $\text{CH}_3\text{NH}_3\text{PbI}_3$ in γ -butyrolactone.

The phase composition near the surface of $\text{CH}_3\text{NH}_3\text{PbI}_3$ layers deposited on molybdenum substrates was investigated by grazing incidence X-ray diffraction (GIXRD, Bruker AXS D8 Advance) before and after annealing in vacuum for 30 min at temperatures of 100, 140, and 160 °C (Figures 1(b)–1(e), respectively). For comparison, the GIXRD pattern is also shown for PbI_2 powder (Figure 1(a)).

The GIXRD results reveal $\text{CH}_3\text{NH}_3\text{PbI}_3$ characteristic peaks at 14.04, 28.42, and 43.08 corresponding to the (002), (220), and (330) planes of $\text{CH}_3\text{NH}_3\text{PbI}_3$, respectively, as shown in Figure 1(b). Our calculated lattice parameters for $\text{CH}_3\text{NH}_3\text{PbI}_3$ with a tetragonal unit cell are $a = 8.881 \pm 0.005 \text{ \AA}$ and $c = 12.560 \pm 0.005 \text{ \AA}$ which is in agreement with previous reports.² The size of the $\text{CH}_3\text{NH}_3\text{PbI}_3$

crystallites has been obtained by using the Scherrer equation and amounted to about 30–40 nm. There are no PbI_2 characteristic diffraction peaks for the $\text{CH}_3\text{NH}_3\text{PbI}_3$ layer annealed at 100 °C. In contrast, characteristic diffraction peaks of PbI_2 appeared after annealing of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ layer at 140 and 160 °C. The appearance of the PbI_2 phase correlated with the appearance of a signature at about 510 nm in optical reflection measurements performed with an integrating sphere.

Modulated SPV spectra were measured⁴ in vacuum at a modulation frequency of 8 Hz. Illumination was performed with a halogen lamp and a quartz prism monochromator. In-phase and phase-shifted by 90° SPV signals were detected with a high-impedance buffer and a double phase lock-in amplifier. To form the measurement capacitor a clean mica sheet (thickness about 20–30 μm) was gently pressed between the sample surface and the cylindrical electrode coated with $\text{SnO}_2\text{:F}$. The samples were heated in vacuum to temperatures up to 220 °C and characterized *in situ* after cooling down to 30 °C. As remark, the mica sheets showed a haze after heating due to partial mass transfer from the substrate onto the mica sheets. Therefore a fresh mica sheet has been taken for each new measurement.

A $\text{CH}_3\text{NH}_3\text{PbI}_3$ layer was successively heated and cooled down to 30 °C. Figure 2 depicts spectra of the in-phase and phase-shifted by 90° SPV signals measured at the as-deposited layer and after successive heating to 60, 100, and 140 °C. The in-phase SPV signal of the as-prepared $\text{CH}_3\text{NH}_3\text{PbI}_3$ layer was negative and set on at photon energy of 1.5 eV corresponding to the band gap of $\text{CH}_3\text{NH}_3\text{PbI}_3$. The SPV spectra of the as prepared $\text{CH}_3\text{NH}_3\text{PbI}_3$ layer correspond to a p-type doped semiconductor with a depletion region at the surface. After heating to 60 °C the shapes of the SPV spectra remained unchanged while the maximum in-phase and phase-shifted by 90° SPV signals increased from -272 to $-376 \mu\text{V}$ and from 110 to 183 μV , respectively. After heating to 100 °C signs of the in-phase and phase-shifted by 90° SPV signals changed between 1.56 and 2.04 eV and between 1.58 and 1.80 eV, respectively. The reduction of the signal heights and the change of the signs give evidence for the onset on surface chemical reactions changing the surface electronic properties. After heating to 140 °C the in-phase SPV signals were positive up to photon energies of 2.42 eV and negative for higher

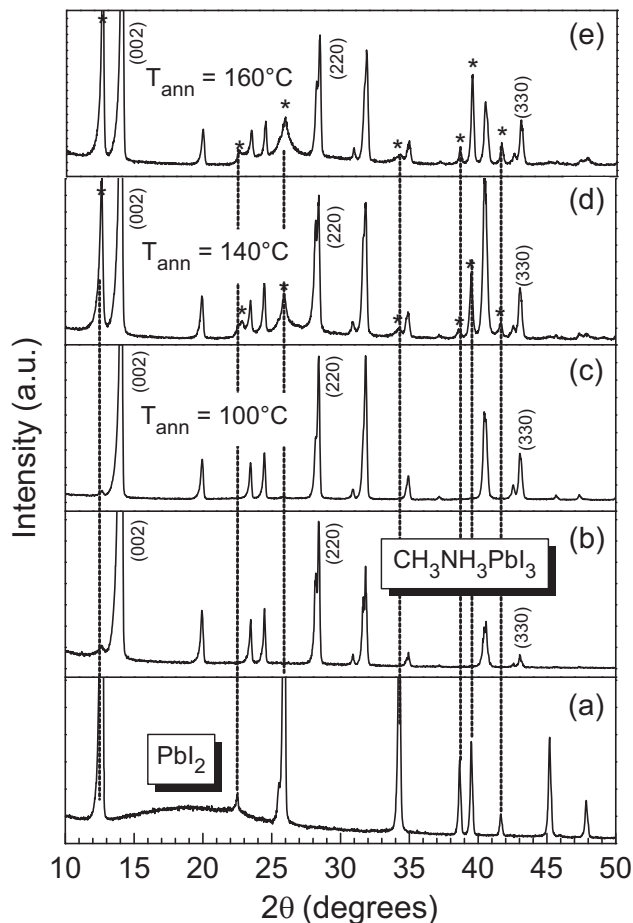


FIG. 1. Grazing incidence x-ray diffraction pattern of PbI_2 powder and of $\text{CH}_3\text{NH}_3\text{PbI}_3$ layers before and after annealing at 100, 140, and 160 °C ((a)–(e), respectively). The dashed lines mark diffraction peaks of PbI_2 .

photon energies while the phase-shifted by 90° SPV signals were negative up to photon energies of 2.52 eV and positive for higher photon energies, i.e., the direction of modulated charge separation changed in comparison to the as prepared and heated to 60 °C samples. Further, after heating to 140 °C a

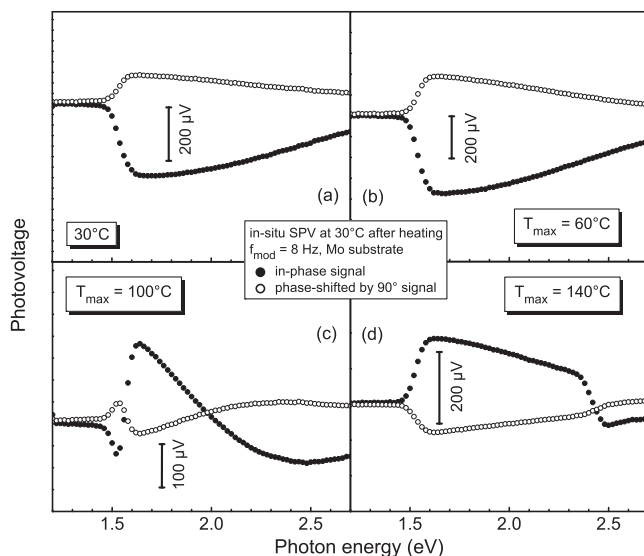


FIG. 2. Modulated surface photovoltage spectra of the in-phase (filled circles) and phase-shifted by 90° (open circles) signals measured at 30 °C on an as-prepared $\text{CH}_3\text{NH}_3\text{PbI}_3$ layer (a) and on $\text{CH}_3\text{NH}_3\text{PbI}_3$ layers after heating to maximum temperatures of 60 °C (b), 100 °C (c), and 140 °C (d).

strong change of the SPV spectra set on at photon energy of 2.36 eV which corresponds to the band gap of a new phase appearing during heating and which is in very good agreement with the band gap of PbI_2 (Ref. 5) and with our results obtained by GIXRD. As a remark, there is now straight forward interpretation of the change of the sign of the modulated SPV signals due to the complexity of transport phenomena and charging/discharging of defect states (see, for example, Refs. 6 and 7).

In contrast to conventional semiconductors such as silicon, there was a mass transfer from the $\text{CH}_3\text{NH}_3\text{PbI}_3$ layer onto the mica sheet during heating. In order to eliminate the influence of material transferred onto the mica sheet during heating, *ex situ* SPV measurements were performed with a fresh mica sheet replacing the mica sheet which has been used during heating experiments. Figure 3 shows the spectra of the photovoltage amplitude, which is the square root of the sum of the squared in-phase and phase-shifted by 90° SPV signals, after heating to 60, 100, 140, and 160 °C. After heating to 100 °C, the PV amplitude decreased for photon energies below 1.5 eV by a factor of 4–5 in comparison to the sample heated up to 60 °C whereas the PV amplitude increased by a factor of about 1.5 for photon energies above 1.6 eV. This behavior is a strong indication for passivation of surface defects at $\text{CH}_3\text{NH}_3\text{PbI}_3$ surface during moderate heating. On the other hand, after heating to 140 °C, the PV amplitude increased by a factor of about 5 for photon energies below 1.4 eV and by a factor of about 11 or 7 at 1.6 or 1.7 eV, respectively, in comparison to the sample heated up to 60 °C. After heating to 160 °C, the PV amplitude increased by a factor of about 20–22 for photon energies below 1.5 eV and by a factor of about 15–16 at photon energies above 1.6 eV in comparison to the sample heated up to 60 °C. The stronger increase of the PV amplitude related to charge separation from defect states after heating at 160 °C shows that defect formation at the $\text{CH}_3\text{NH}_3\text{PbI}_3/\text{PbI}_2$ interface can become significant.

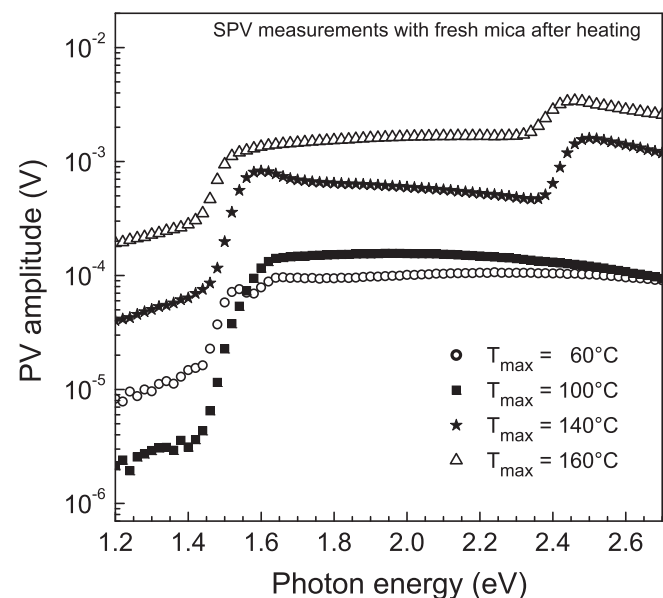


FIG. 3. Spectra of the PV amplitude measured with a fresh mica sheet replacing the mica sheets after heating to $T_{\text{max}} = 60, 100, 140,$ and 160 °C (open circles, filled squares, filled stars, and open triangles, respectively).

For comparison, the open circuit voltage of solar cells based on a $\text{CH}_3\text{NH}_3\text{PbI}_3$ absorber increased after heating at 100°C and continued to increase even after heating at 160°C while the short circuit current density decreased after heating at 160°C (Ref. 8) due to an increased transformation rate of $\text{CH}_3\text{NH}_3\text{PbI}_3$ to PbI_2 . Further, mass transfer from $\text{CH}_3\text{NH}_3\text{PbI}_3$ layers to mica sheets gives evidence for the high mobility of ionic species in $\text{CH}_3\text{NH}_3\text{PbI}_3$ layers. This is beneficial for the formation of intimate contact regions in solar cells based on $\text{CH}_3\text{NH}_3\text{PbI}_3$ absorber layers. As remark, solar cells based on $\text{CH}_3\text{NH}_3\text{PbI}_3$ absorber layers have a tremendous strategic potential exceeding that of most photovoltaic absorber materials⁹ and the formation of intrinsic passivating layers on $\text{CH}_3\text{NH}_3\text{PbI}_3$ layers is a prerequisite for their broad application.

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