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Atittaya Naikaew, Pongthep Prajongtat, Martha Ch. Lux-Steiner, Marisa Arunchaiya, and Thomas Dittrich

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Role of phase composition for electronic states in CH$_3$NH$_3$Pbl$_3$ prepared from CH$_3$NH$_3$I/PbCl$_2$ solution

Atittaya Naikaew,1,2 Pongthep Prajongtat,1,2 Martha Ch. Lux-Steiner,1 Marisa Arunchaiya,2 and Thomas Dittrich1,a)

1Helmholtz-Center Berlin for Energy and Materials, Institute of Heterogeneous Materials, Hahn-Meitner-Platz 1, D-14109 Berlin, Germany
2Department of Materials Science, Faculty of Science, Kasetsart University, Bangkok 10900, Thailand

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High solar energy conversion efficiencies have been demonstrated for solar cells with absorbers based on organic-inorganic hybrid lead halide perovskites, especially CH$_3$NH$_3$Pbl$_3$ (MAPbI$_3$). However, strong degradation makes the successful application of perovskite solar cells impossible to date. A better understanding of defect formation and degradation is crucial for the successful development of stable related solar cells.

Shallow acceptor and donor traps with low formation energy and flexible properties allowing for intrinsic p- and n-type doping have been observed by theoretical analysis. This unusual defect physics of MAPbI$_3$ is in contrast, for example, to conventional CuInSe$_2$ thin-film absorbers for which the formation energy of acceptors is much lower than for donors. It has been shown experimentally that an excess or deficit of CH$_3$NH$_3$I (MAI) in the perovskite precursor solution containing MAI and PbI$_2$ caused p- or n-type doping, respectively, of MAPbI$_3$. Degradation of MAPbI$_3$ almost occurs at room temperature and leads to the formation of PbI$_2$. The resulting MAPbI$_3$/PbI$_2$ interface is well passivated, enables the transfer of electrons but blocks the transfer of holes.

Mild annealing conditions at about 100°C are applied for numerous preparation processes of MAPbI$_3$ layers used for high efficiency solar cells. Furthermore, the addition of chlorine into the precursor led to improved performance of related solar cells. The application of MAI or MACl and PbCl$_2$ or PbI$_2$ precursors causes coexisting phases and phase transformations involving the formation of MAPbCl$_3$, MAPbI$_3$, MACl, and PbI$_2$ as well as of un-identified phases. MAPbI$_3$ was present as the dominant phase after all annealing times, and MAPbCl$_3$, MACl, and un-identified phases disappeared and PbI$_2$ appeared after long annealing times. Therefore, the behavior of electronic states near and below the band gap of MAPbI$_3$ can be studied for samples with different phase compositions by following the preparation conditions described in the works of Song et al. and Unger et al.

In this work, MAPbI$_3$ has been prepared from MAI and PbCl$_2$ precursors with a mole ratio of 3 to 1 in N,N-dimethylformamide (DMF) and annealed at 100°C for different times in order to investigate electronic properties of MAPbI$_3$ changing from p- to n-type doping in correlation with the phase composition. Grazing incidence x-ray diffraction (GIXRD) and modulated surface photovoltage (SPV) spectroscopy were applied for the characterization of the phase composition and of the electronic properties of the layers, respectively. In modulated SPV measurements, a semitransparent electrode (SnO$_2$:F) is gently pressed on a mica sheet which has been placed on the sample before. Therefore, modulated SPV measurements do not require any contact preparation so that the undisturbed MAPbI$_3$ samples were investigated after annealing. As remark, GIXRD and SPV measurements can be well correlated since the information depths are of the same order (penetration depth for GIXRD and diffusion length of photo-generated charge carriers several 100 nm).

A 40 wt. % perovskite precursor solution was prepared by dissolving MAI (Dyesol) and PbCl$_2$ (Carl Roth Germany) with a 3:1 mole ratio in DMF (Sigma Aldrich). After stirring the precursor solution at 60°C overnight, the solution was spin coated onto molybdenum coated glass substrates (1000 rpm for 10 s followed by 3000 rpm for 60 s). The layer thickness was about 300 nm. The layers were annealed at
100 °C in a N2-filled glovebox for 0, 15, 30, 45, 60, and 90 min. After annealing, the samples (size 25 × 25 mm²) were cut into two separate samples and stored in nitrogen filled envelopes in the glovebox.

The modulated (modulation frequency 8 Hz) SPV measurements were carried out in vacuum (2 × 10⁻⁵ mbar) in the fixed capacitor arrangement14 (see also the inset of Figure 2) in the day of sample preparation. Illumination was performed with a halogen lamp and a quartz prism monochromator (intensity on the sample about 0.8 mW/cm² at 830 nm). In-phase and phase-shifted by 90° SPV signals were detected with a high-impedance buffer and a double phase lock-in amplifier (EG&G 5210).

Figure 1 shows the GIXRD (angle of incidence 0.9°) patterns of the as-deposited layer and of the layers annealed for different times. As remark, little peaks related to molybdenum were still detected after layer deposition (not shown). The (110) diffraction peak of MAPbI₃ at around 14.22° or 14.12° (Ref. 15) appeared for the as-deposited and for all annealed samples, respectively. The peak height at 14.12° increased with the increase in annealing time up to 60 min and decreased slightly for the longer annealing time. The (100) diffraction peak of MAPbCl₃ at around 15.67° (Ref. 16) increased with the increase in annealing time up to 30 min, decreased with further increasing annealing time, and disappeared for the sample annealed for 90 min. The fact that the peak positions at 14.12° and 15.57° remained constant gave evidence for segregation of the pure MAPbI₃ and MAPbCl₃ phases. A tiny diffraction peak at 17.5° related to MACl could be observed for the as-deposited sample and disappeared for annealing times above 30 min. The (001) diffraction peak of PbI₂ at 12.65° (Ref. 16) appeared after annealing for 60 min and increased strongly after annealing for 90 min. The un-identified diffraction peaks at around 12.0°, 16.7°, and 18.1°, denoted by NN1, NN2, and NN3 in Figure 1, respectively, were probably related to ongoing crystallization of precursors with a high amount of residual solvent decreasing for annealing times longer than 30 min and disappearing after annealing for 90 min. The decrease in the amount of MAPbCl₃ and MACl was caused by evaporation of MACl.9 The decrease of the amount of MAPbI₃ and the increase of the amount of PbI₂ were caused by ongoing evaporation of MAI.

Figure 2 shows the in-phase (x-signal) and phase-shifted by 90° (y-signal) SPV spectra of the as-deposited sample (a) and of the samples annealed for 15, 30, 45, 60, and 90 min ((b)-(f), respectively). As remark, the x- and y-signals are related to the responses following fast or slowly, respectively, in relation to the modulation period. All samples showed the dominant onset of SPV signals at about 1.5 eV, i.e., at the band gap of MAPbI₃.13 This is in agreement with the existence of the MAPbI₃ phase detected in the XRD measurements.

The x-signals were negative for the as-deposited sample and for the samples annealed for 15, 30, and 45 min and positive for the samples annealed for 60 and 90 min. As a remark, a negative (positive) sign of the x-signals means that photo-generated electrons are separated preferentially towards the external surface (internal interface). The surface regions of moderately doped semiconductors are in depletion. Therefore, the change of the sign of the x-signals marked the change from p- to n-type doped MAPbI₃.

The change of the sign of the x-signals coincided with the appearance of the PbI₂ phase, whereas the MAPbCl₃ and the un-identified phases were still present after annealing for 60 min (see Figure 1). As a remark, a signature of the band gap of PbI₂ (around 2.3 eV) just appeared in the spectra of the first derivative of the x-signals. Intrinsic n-type doping of MAPbI₃ was assigned to a deficiency of MA and I leading preferentially to interstitials of MA and vacancies of I which have the lowest formation energies.3 Self-doping in MAPbI₃ by excess (p-type) or deficiency (n-type) of MA and I has been demonstrated by Hall-effect measurements.9 As a conclusion, the appearance of PbI₂ at the surface of MAPbI₃ is a clear indication for the deficiency of MA and I in the region near the interface and therefore for n-type doping of MAPbI₃.

The sign of the y-signals was positive for the as-deposited sample and changed to negative for the samples...
annealed for 15 and 30 min (photon energies between 1.6 and 3.2 eV); i.e., the x- and y-signals got the same sign. The x- and y-signals had also the same sign for the samples annealed for 60 and 90 min. As remark, the x- and y-signals had opposite signs for excitation of photo-generated charge carriers from defect states (photon energies below 1.55 eV).

The same sign of x- and y-signals means that there are two mechanisms of charge separation with opposite direction.

Evaporation of MACl and later of MAI starts with beginning annealing. Therefore, annealing leads to the formation of defect states near the surface of MAPbI3 at which photo-generated holes can be trapped. Similarly, decomposition of MAPbI3 at the MAPbI3/PbI2 interface leads to the formation of defect states at which electrons can be trapped.

The negative and positive x-signal heights have a maximum at 2.4 and 1.7 eV for the samples annealed for 15 and 90 min, respectively. The x-signals at 1.7 and 2.4 eV increased from −0.15 and −0.17 for the as-deposited sample to −0.50 and −0.87 mV, respectively, for the sample annealed for 15 min. This strong increase correlated with the increase of the XRD pattern for MAPbI3 and was therefore related to ongoing formation of MAPbI3.

The x-signals at 1.7 and 2.4 eV decreased to −0.3 and −0.57 and to −0.15 and −0.2 mV for the samples annealed for 30 and 45 min, respectively. At the same time, MACl disappeared. The decrease of the negative x-signals was related to the ongoing evaporation of MACl and MAI and therefore to the decrease of the concentration of acceptors.

The x-signals at 1.7 and 2.4 eV increased from 0.71 and 0.44 mV for the sample annealed for 60 min to 1.73 and 0.79 mV, respectively, for the sample annealed for 90 min. The increase of the positive x-signals was related to the ongoing evaporation of MAI and formation of PbI2 and therefore to the increase of the concentration of donors.

A shoulder or little peak very close to the band gap of MAPbI3 can be well distinguished in the spectra of the x-signals for the as-deposited samples and for the samples annealed for 15, 30, and 45 min, i.e., for the p-type doped samples. The disappearance of the related peak or shoulder in the n-type doped sample gave evidence for excitation of electrons from shallow acceptor states such as lead vacancies or iodine interstitials (have low formation energy and electronic states slightly above the valence band edge) into the conduction band of p-type doped samples. Furthermore, one has to keep in mind that a high density of shallow acceptors can distort the onset energy of the SPV spectrum. The shallow donors in n-type doped MAPbI3 with low formation energy (MA interstitial and iodine vacancy) have states within the conduction band what makes them difficult to be distinguished.

The significance of deep defect states can be described, for example, by the ratio of the PV amplitudes, i.e., the square root of the sum of the squared x- and y-signals, measured at 1.1 and at 1.7 eV (R1.1 eV/R1.7 eV). Figure 3 summarizes the dependence of R1.1 eV/R1.7 eV on the annealing time together with the regions of the phases detected by XRD. For the as-deposited sample and for the samples annealed for 15, 30, and 45 min, the value of R1.1 eV/R1.7 eV increased with increasing annealing time. The value of R1.1 eV/R1.7 eV dropped strongly down by more than one order of magnitude for the sample annealed for 60 min and increased again for the sample annealed for 90 min. The minimum of the value of R1.1 eV/R1.7 eV correlated with the transition from p-type to n-type doping and with the appearance of PbI2.

Evaporation of MAI caused the formation of structural defects near the surface of p-type doped MAPbI3. Structural defects near the surface of MAPbI3 merged to a new phase, i.e., PbI2, at the transition point to n-type doping. With further annealing, HI, having also low dissociation energy, evaporated and created damage of the lattice near the developing MAPbI3/PbI2 interface. This result shows that there is only a narrow window for optimization of the electronic properties of MAPbI3 with respect to doping and a minimum of defect states.

The phase composition practically does not have influence on the electronic states being important for the electronic properties of MAPbI3 excluding the formation of PbI2 being an indication for n-type doping. The strong dependence of the doping of MAPbI3 on continued evaporation of MAI and HI makes the reproducibility of electronic properties of MAPbI3 rather challenging in relation to the preparation and to the stability of solar cells with MAPbI3 absorbers. Therefore, sinks for MAI and/or HI have to be minimized or avoided for reaching a high long-term stability of solar cells with MAPbI3 absorbers. One opportunity can be, for example, the dedicated stabilization of bond configurations at interfaces with MAPbI3, for example, by introducing ammonium valeric acid iodide. Another opportunity can be the formation of dense interfaces between MAPbI3 and inorganic contact layers. As a remark, it seems rather harsh to avoid diffusion of HI in polymer layers and to get high long-term stability of solar cells with MAPbI3 absorbers including interfaces between MAPbI3 and organic contact layers. However, detailed investigations on the stability of interfaces with MAPbI3 are required, whereas SPV measurements can be very helpful.
As a remark, surface coverage is a major issue for the performance of solar cells based on MAPbI\textsubscript{3} as stated, for example, by Eperon. In this work, the coverage of Mo with MAPbI\textsubscript{3} was above 95\%, i.e., pinholes could not be avoided yet. However, the obtained SPV results are not affected by pinholes. Furthermore, the evolution and passivation of defects depend sensitively on the ambient. For example, annealing in air resulted in less disorder of MAPbI\textsubscript{3} in comparison to annealing in nitrogen, whereas the decomposition rates are strongly enhanced in air. This is not surprising since adsorbed water molecules can decompose at semiconductor surfaces and resulting hydrogen or hydroxide can passivate defects or enhance corrosion, respectively. It can be expected that the increased decomposition rate of MAPbI\textsubscript{3} in humid ambient will lead to a reduced onset time of the transition from p- to n-type doping.

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