Light-Induced Degradation of CH₃NH₃PbI₃ Hybrid Perovskite Thin Film

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ABSTRACT: The stability of CH₃NH₃PbI₃ was investigated by observing the degradation in a coevaporated film irradiated by a blue laser in ultrahigh vacuum. X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM) were employed to investigate the effects of irradiation on the surface. The core levels of CH₃NH₃PbI₃ were observed to shift toward a higher binding energy (BE) during the irradiation, suggesting that the surface became more n-type. A new metallic Pb component in the XPS spectrum appeared after 120 min of irradiation, indicating that the film had started to decompose. The decomposition saturated after about 480 min of irradiation when the ratio of metallic Pb to total Pb was about 33%. Furthermore, the film no longer continued after irradiation, as the elements gold and oxygen from the substrate were detected by XPS. SEM images also show a roughened surface after irradiation. The results strongly indicate that CH₃NH₃PbI₃ is sensitive to the laser irradiation and that the light induced decomposition is a self-limiting process.

INTRODUCTION

Organic photovoltaics, dye-sensitized solar cells, and colloidal nanocrystal solar cells have widely been investigated in recent years as an important source of renewable energy. The most critical factors for the utility of solar cells are their cost of production, power conversion efficiency (PCE), and the sustainability of the source materials. Recently, organic−inorganic halide perovskites have attracted considerable attention as a light-harvesting material for new solar cells, offering both low cost and reasonably high PCE compared with that of silicon, dye-sensitized, and other standard solar cells. Hybrid perovskite was first used in a dye-sensitized solar cell by Miyasaka and co-workers in 2009 with a PCE of 3.8%. Kim and co-workers later reported a solid-state hybrid perovskite solar cell with a PCE of 9.7% in 2012. Soon after that, hybrid perovskite solar cells with a planar heterojunction structure were also reported with a PCE of 5%, and have since continued to rapidly increase to as high as a certified value of 22.1%. Hybrid perovskite solar cell’s PCEs are presently quite close to that of the standard crystalline silicon solar cells.

Hybrid perovskite films are mainly fabricated by either solution based spin coating or thermal evaporation. The spin coating method is a simpler process and of lower production cost than that of the latter, and it is therefore popularly used for device fabrication. Surface and interface investigations of spin-cast films have produced information important for understanding the performance of devices fabricated with spinning. However, the surface composition of spin coated films usually deviates significantly from the stoichiometric ratio. Alternatively, the thermal evaporation method can produce smoother films with the correct surface stoichiometry and crystal structure, which is essential for surface sensitive analytical investigations on the fundamental material properties of the hybrid perovskite.

Although the PCE of the hybrid perovskite solar cell has already reached over 20% in laboratory, the stability of the light-harvesting film (CH₃NH₃PbX₃, X = I, Cl, Br) remains a critical issue for the eventual success of commercial applications. Early work attributes illumination induced degradation of hybrid perovskite solar cells to the TiO₂ layer in the device. Murugadoss et al. investigated light illumination stability of thin hybrid perovskite films on different substrates and found a strong substrate dependence. Bryant et al. demonstrated light illumination played a key role in hybrid perovskite degradation when exposed to gases and ambient air. Applying simultaneous luminescence and electron
microscopy, Yuan et al. found that light-induced degradation results in material decomposition but little photoluminescent (PL) spectral shifts. On the other hand, Merdasa et al. observed rapid degradation and continuous PL spectral blue shift of hybrid perovskite nanocrystals using super-resolution luminescence microspectroscopy. We have previously shown that CH₃NH₃PbI₃ is sensitive to moisture and decomposes rapidly after reaching a threshold of 2 × 10⁻¹⁰ Langmuir of water exposure.

In this work, we present our investigation of the effects of laser irradiation on CH₃NH₃PbI₃ films using XPS and SEM. The films were prepared by thermal evaporation, with proper stoichiometry, uniformity, and crystal structure. After laser irradiation for only 120 min by blue light of wavelength 408 nm, more details of the instrument and the evaporation procedure are described previously in ref28.

The sample was transferred into the analytical chamber of base pressure 1 × 10⁻⁷ Torr, which was equipped with an X-ray monochromator with a high-throughput bent quartz crystal providing monochromatic Al Kα radiation (1486.6 eV). The irradiation light used for exposure came from a semiconductor laser with a wavelength of 408 nm. The laser’s output power was 20 mW and the irradiation intensity on the sample was about 6.8 × 10⁻³ W/mm², which was about 7 times the commonly used AM1.5 irradiation (1000W/m²). The laser irradiation covered an oval shaped area approximately 1.4 × 2.6 mm, and the probing X-ray spot was about 0.8 × 1.4 mm in size. After each timed irradiation, we immediately performed XPS measurements on both the laser irradiated spot and another nonirradiated spot on the surface. Precise control of the sample position was guided by an optical microscope attached to the chamber. All other windows on the chamber were shaded to avoid the light influence from the outside.

**Data Process and SEM Images.** The valence band maximum (VBM) of the film is determined by the intersection of linear extrapolations of the leading edge and of the background. The core level peaks were fitted with commercial software Origin 6.0. Shirley-type corrections were performed to remove the secondary electron background and the ratio of Lorentzian and Gaussian line shapes was not fixed during the peak fitting. The atomic ratio of the film was calculated by comparing the areas of the fitted curves divide by their elemental sensitivity factor. At the end of the experiment for a total irradiation time of 2210 min, the sample was taken out of the chamber and was investigated immediately with a Zeiss Auriga SEM located at the University of Rochester’s UR-nano center.

## EXPERIMENTAL SECTION

**Film Fabrication.** The film evaporation and XPS measurements were performed in a modified Surface Science Laboratories’ SSX-100. The base pressure of the evaporation chamber is typically 1 × 10⁻⁷ Torr. PbI₂ (Shanghai Zhenpin Technology Co.,99%) and CH₃NH₃I (Wuhan Crystal Solar Laboratories) were mixed in a molar ratio of N:I:Pb = 1.10:3.28:1.00 and 1.09:3.26:1.00 at the laser irradiation. The uniformity of the film was also destroyed by the irradiation as the elements from the substrate, gold and oxygen, were detected by XPS and roughening of the surface was shown by SEM. The results provide important insight for the design of hybrid perovskite-based solar cells.

**Irradiation and XPS Measurements.** The sample was then transferred into the analytical chamber of base pressure 1 × 10⁻¹⁰ Torr, which was equipped with an X-ray monochromator with a high-throughput bent quartz crystal providing monochromatic Al Kα radiation (1486.6 eV). The irradiation light used for exposure came from a semiconductor laser with a wavelength of 408 nm. The laser’s output power was 20 mW and the irradiation intensity on the sample was about 6.8 × 10⁻³ W/mm², which was about 7 times the commonly used AM1.5 irradiation (1000W/m²). The laser irradiation covered an oval shaped area approximately 1.4 × 2.6 mm, and the probing X-ray spot was about 0.8 × 1.4 mm in size. After each timed irradiation, we immediately performed XPS measurements on both the laser irradiated spot and another nonirradiated spot on the surface. Precise control of the sample position was guided by an optical microscope attached to the chamber. All other windows on the chamber were shaded to avoid the light influence from the outside.

**RESULTS AND DISCUSSION**

**Evidence of Degradation.** Figure 1a shows the survey scan of the film before and after laser irradiation. For comparison, the scan of nonirradiated position is also shown in Figure 1b. (see Figure S1 in the Supporting Information for more survey scans) There were no other obvious elements in the as-evaporated survey scan except for C, N, I, and Pb, indicating that the CH₃NH₃PbI₃ film was uniform and free of contamination. The atomic ratios of the as-evaporated film are N:I:Pb = 1.10:3.28:1.00 and 1.09:3.26:1.00 at the laser illuminated and nonilluminated spot, respectively. Carbon was not shown here because the contamination from the substrate was difficult to eliminate. The ratio of N:I:Pb can demonstrate a reasonably good stoichiometry. The atomic ratio also shows the surface uniformity. The polycrystallinity of the film thus prepared has been demonstrated previously. As shown in Figure 1a, after only 240 min of irradiation, the Au 4f and O 1s peaks are clearly visible, indicating that the film was no longer uniform. The presence of Au and O suggests that the photoemitted electrons were coming from the underlying gold substrate, which had water or oxygen adsorbrates on it because it was not sputter cleaned prior to the evaporation. At
the end of the experiment when the sample was irradiated for 2210 min, the intensity of the Au 4f and O 1s peaks further increased. In contrast, the XPS spectra from the nonirradiated position show no gold or oxygen, as can be seen in Figure 1b. The XPS survey scan results strongly suggest that the CH₃NH₃PbI₃ film is sensitive to laser irradiation, and the high intensity (∼7 times of AM 1.5) of the laser may accelerate the degradation process. In addition, we found that after only about 120 min of laser irradiation, the color of the exposed spot became visibly lighter than that of the nonirradiated region.

Detailed Analysis. In parts a and b of Figure 3, we present the valence band of the CH₃NH₃PbI₃ film during the experiment. Figure 3a is from the laser irradiated position, while Figure 3b is from the nonirradiated one. We found that the valence band maximum (VBM) increased by about 0.4 eV, from 0.85 eV initially to 1.25 eV after the total 2210 min of irradiation. The shift seemed to be saturated after about 480 min of irradiation. The band gap of CH₃NH₃PbI₃ is known to be around 1.55 eV, so the “as prepared film” was a slightly n-type one to begin with. The shift toward a high binding energy (BE) indicated the film became more n-type during the laser irradiation. Meanwhile at the nonirradiated position, no obvious changes can be seen in the VBM region. Another feature to notice is that after only 120 min of laser irradiation, a new peak at about 6.5 eV begins to appear in the irradiated spectrum. This indicates the existence of oxygen on the surface, as the film is in the ultrahigh vacuum chamber and is not sensitive to oxygen exposure. The oxygen could only come from contaminants on the underlying substrate since the substrate surface was not cleaned by Ar sputtering prior to evaporation of the CH₃NH₃PbI₃ film. This further provides evidence that parts of the substrate were uncovered as photoemitted electrons from the underlying gold substrate could be seen.

Shown in parts c and d of Figure 3 are the Pb 4f₇/₂ spectra from laser irradiated and nonirradiated positions, respectively. The BE of as-evaporated Pb 4f₇/₂ is about 138.08 eV, which is consistent with the previous report. As the laser irradiation progresses, changes can be observed in the core level position. After about only 120 min of laser irradiation, a new peak at...
about 136.87 eV in Pb 4f7/2 began to appear (Figure 3c) and it grew in intensity as the irradiation continued. The new Pb 4f7/2 peak is that of metallic Pb, and it seems synchronized to the 6.5 eV peak in the VBM region. In contrast, the Pb 4f7/2 spectra of the nonirradiated position in Figure 3d present no discernible spectral changes.

CH3NH3PbI3 films are usually known to decompose into PbI2 and other components. PbI2 is photosensitive and can usually decompose into PbO and I2 in the presence of moisture and light. In our case, the film was in ultrahigh vacuum (UHV), where there was no H2O or oxygen. It is apparent that the PbI2 released by laser irradiation further decomposes into metallic lead and iodine by irradiation alone, leading to the new peak in Pb 4f7/2 at 136.87 eV as shown in Figure 3c. Iodine released in this photochemical reaction will sublime to vacuum, leaving the metallic Pb with the remaining hybrid perovskite. Previous reports have also found metallic lead in as fabricated CH3NH3PbI3 films (especially for spin-cast films), and it was considered to be related to the excessive precursor PbI2 and the removal of I2. The binding energy of metallic Pb is reported to be 137.0 eV, which is very close to that of the new component at 136.87 eV after irradiation. The metallic lead will act as quenching centers of excitons, evidenced by the detrimental effect it has on the photoluminescence quantum efficiency. As a result, this degradation process will have a serious effect on the device PCE. On the other hand, the degradation process may be kinematically limited in the bulk of hybrid perovskite or in a well sealed device when the volatile components in the reaction are not allowed to escape as easily as in a vacuum.

Beside the decomposition, we also found an ∼0.46 eV shift of perovskite Pb 4f7/2 from 138.08 to 138.54 eV in the irradiated position (see Figure 3c). This shift of the perovskite Pb 4f7/2 is consistent with that of the VBM, supporting the notion that the film has become more n-doped. The n-doping may be due to the fact that the film has become Pb rich, similar to the case when a hybrid perovskite is annealed at high temperature.

Further support of the n-doping of the CH3NH3PbI3 film can be obtained by observing the shifts of the other core levels. Should there be n-doping, the movement of the Fermi Level within the band gap toward the conduction band minimum will result in a rigid shift in all the energy levels in the semiconductor. The evolution of I 3d5/2 and N 1s at laser irradiated (Figure 4, parts a and c) and nonirradiated (Figure 4, parts b and d) position are both shown in Figure 4 to have a comparison. Dotted lines and short bars are marked to show the core level shift. For the laser irradiated position, the I 3d5/2 had a ∼0.51 eV shift (Figure 4a) toward higher binding energy from 618.97 to 619.48 eV after the irradiation. The shift also seems to be already saturated after 480 min of irradiation. A similar shift can also be seen for N 1s in Figure 4c. The shift is about the same as that of Pb 4f7/2 considering the instrument uncertainty. We can thus conclude that these shifts in the core levels were caused by the movement of the Fermi level in the film, which is further consistent with the VBM shift shown in Figure 3a. We also found a serious intensity decrease of N 1s after irradiation shown in Figure 4c, indicating the decomposition of the film and the escape of N. For the nonirradiated position, such shifts were again not observed (Figure 4, parts b and d).

**Mechanism of Degradation.** On the basis of the above discussions, we found that the results agree with a mechanism of degradation. First, CH3NH3PbI3 decomposed into PbI2 and other volatile components, and then PbI2 further decomposed into metallic Pb and I. The proposed degradation procedure can be expressed as the following:

\[
\text{CH}_3\text{NH}_3\text{PbI}_3 \xrightarrow{\text{light}} (\text{CH}_2\cdots) + \text{NH}_3 + \text{HI} + \text{PbI}_2
\]

(1)

\[
\text{PbI}_2 \xrightarrow{\text{light}} \text{Pb} + \text{I}_2
\]

(2)

The volatile components, NH3 and HI should fly away from the surface, and so should the iodine by sublimation, leaving unreacted CH3NH3PbI3, metallic Pb, and carbon hydrocarbonaceous species on the surface. Without a means of stabilizing the hybrid perovskite thin film, the degradation will severely limit the ability of this material to be used in the consumer market as a light absorbing layer in a solar cell.

The detailed curve fitting of Pb 4f7/2 is shown in Figure 5a. The dotted line and short bars clearly show the appearance of metallic Pb at 136.87 eV and the 0.46 eV shift of perovskite Pb 4f7/2 toward higher binding energy. It is clear that the shift of the perovskite Pb 4f7/2 was already saturated after about 480 min of irradiation, in contrast to the stationary metallic one. Shown in Figure 5b is a plot of the ratio between metallic Pb and total Pb during the laser irradiation, which is calculated from the areas under the fitted curves. A select number of fitted Pb 4f7/2 curves are shown in Figure 5a. It increased from 26% after 120 min to 33% after 480 min of irradiation, and then the
ratio remained almost constant. This indicated that the degradation saturated after laser irradiation of about 480 min.

Parts a and b of Figure 6 show the atomic ratio change of the laser irradiated position and the nonirradiated position, respectively. For the laser exposed position, the ratio of N and I decreased quickly, from N:I:Pb = 1.10:3.28:1.00 to 0.48:1.82:1.00 after 480 min of irradiation, at which point the ratios became relatively constant. For the nonexposed position, the ratio of N and I also decreased slightly, from N:I:Pb = 1.09:3.26:1.00 to 0.85:2.82:1.00 at the time corresponding to 480 min of irradiation. The small reduction of the N-to-Pb ratio at the nonirradiated position is likely to be caused by the probing X-ray used for XPS. Reduction by extended exposure to vacuum can be ruled out as we further checked a new position on the sample that was neither irradiated by laser or X-ray after the laser exposure measurements, and found that the atomic ratio to be N:I:Pb = 1.03:3.27:1.00, which was almost the same as the initial ones of laser irradiated and nonirradiated position.

The amount of reduction of N and I by laser radiation alone can be calculated by comparing the ratios of irradiated and nonirradiated positions presented in Figure 6. The N ratio is reduced by 0.38 and that of I by 1.02 by 480 min of laser irradiation after eliminating the contribution from the probing X-ray. Reduction by extended exposure to vacuum can be ruled out as we further checked a new position on the sample that was neither irradiated by laser or X-ray after the laser exposure measurements, and found that the atomic ratio to be N:I:Pb = 1.03:3.27:1.00, which was almost the same as the initial ones of laser irradiated and nonirradiated position.

The amount of reduction of N and I by laser radiation alone can be calculated by comparing the ratios of irradiated and nonirradiated positions presented in Figure 6. The N ratio is reduced by 0.38 and that of I by 1.02 by 480 min of laser irradiation after eliminating the contribution from the probing X-ray. Given the stoichiometric ratio of CH$_3$NH$_3$PbI$_3$ and that the metallic Pb is now 33% of the total, we can deduce that within the uncertainty of the measurement, about 33% of the CH$_3$NH$_3$PbI$_3$ is decomposed at saturation, and all the volatile components left the surface as described in eqs 1 and 2. The total light fluence is $1.96 \times 10^8$ J/m$^2$ at the saturation. The reason for the saturation may be that the exciton quenching centers formed by the metallic lead have effectively quenched all the excitons in the thin film. The formation of the metallic lead requires the sublimation of volatile components, which is kinematically limited by the diffusion process. The decomposition process is then expected to start from the very surface of the CH$_3$NH$_3$PbI$_3$ film.

If we take a simplified model that the outer layer is completely decomposed while the underlying one remains intact, we can estimate the thickness of the decomposed layer, which gives the lower limit of the decomposed region. From the exponential attenuation, the XPS intensity $I_d$ from a given thickness $d$ is

$$I_d = \int_0^d I_0 e^{-x/\lambda} \, dx = I_0 \lambda (1 - e^{-d/\lambda})$$

(3)

where $I_0$ corresponds to the unit emission intensity density and $\lambda$ the electron mean free path.

The ratio of the intensity from the decomposed layer of thickness $d_1$ to that of the whole layer of thickness $d$ is given by

$$\frac{I_{d_1}}{I_d} = \frac{1 - e^{-d_1/\lambda}}{1 - e^{-d/\lambda}}$$

(4)

We can deduce that...
$$d = -\lambda \ln \left[ 1 - \frac{I_d}{I_l} (1 - e^{-d/\lambda}) \right]$$

With $d = 10$ nm (the film thickness), $\lambda = 2.0$ nm, and the intensity ratio of metallic Pb and the total Pb, $I_{dl}/I_d = 0.33$, the degradation thickness $d_1$ caused by laser irradiation is calculated to be 0.82 nm. It should be mentioned that eqs 3–5 are truly valid only for thin films of homogeneous thickness and composition. As the degradation alters the morphology of the film as shown in Figure 1, the degradation thickness thus obtained can only be taken as a rough estimate. Our results may also explain the discrepancy between the PL investigations of the hybrid perovskite degradation by light. In a layered geometry, the light-induced decomposition is limited to the outer surface and the bulk of the material remains intact, thus giving no spectral shift.\(^{26}\) On the other hand, nanocrystals of hybrid perovskite have much larger relative surface area, and the light-induced degradation is fast and the PL spectral shift is continuous as the diffusion process is no longer a limiting factor.\(^{27}\)

A natural question is whether the changes by irradiation reported here are due to heating by the laser beam, as hybrid perovskites are known to be unstable above 85 °C even in inert atmosphere.\(^{36}\) We have carefully analyzed such a possibility and found it unlikely. In our estimate, the gold layer (100 nm) on the silicon substrate acted as a thermal reservoir for the thin CH\(_3\)NH\(_3\)Pb\(_I_3\) film and should have prevented any appreciable heating and corresponding heating degradation despite hybrid perovskite’s extremely low thermal conductance. Following Abbott’s model for the heating effects due to a low power CW laser as we used in the experiment, we calculated a steady state temperature increase of less than 1 K.\(^{35}\) We want to point out that the temperature increase is small because the film is very thin, and appreciable heating may be possible in thicker films or single crystals.\(^{35,36}\) The calculation demonstrates that the decomposition was caused by the irradiation instead of laser heating effects.

**CONCLUSIONS**

We have investigated the effects of laser irradiation on evaporated CH\(_3\)NH\(_3\)Pb\(_I_3\) thin films. After exposing to irradiation for only 120 min by a blue laser with a wavelength of 408 nm and illumination intensity of 6.8 × 10\(^{-3}\) W/mm\(^2\), the film began to decompose. The VBM and the core level were seen to shift toward higher binding energies, indicating an n-type doping during the irradiation. The appearance of metallic Pb and the intensity reduction of N and I demonstrate that the film had decomposed by the laser irradiation. The decomposition saturated after about 480 min of laser irradiation. At saturation, the ratio between metallic Pb and total Pb was about 33%. Correspondingly, N and I were also seen to be reduced by the same fraction due to the laser irradiation. A model of the decomposition is proposed and a lower limit estimate sets the decomposition at approximately 1 nm of the total 10 nm thick film. SEM shows that the surface was roughened and parts of the substrate were uncovered after irradiation because of the stress change caused by the degradation. This research indicates that light can cause and accelerate the decomposition of CH\(_3\)NH\(_3\)Pb\(_I_3\) films. It also indicates that keeping the volatile decomposition products from leaving the surface is necessary for the long-term application of hybrid perovskite solar cells.


(29) Niu, G. D.; Li, W. Z.; Meng, F. Q.; Wang, L. D.; Dong, H. P.; Qiu, Y. Study on the Stability of CH3NH3PbI3 Films and the Effect of