Substrate-dependent Growth of CH$_3$NH$_3$PbI$_3$ Films Deposited by Vacuum Evaporation

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Abstract. CH$_3$NH$_3$PbI$_3$ (MAPbI$_3$) films were prepared by dual-source vacuum evaporation on Au, poly(3,4-ethylenedioxythiophene) (PEDOT), and indium-tin-oxide (ITO) with the similar deposition parameters. The films were characterized with X-ray diffraction (XRD), steady-state photoluminescence (PL) and Raman spectroscopy. The interface electronic structures of co-evaporated MAPbI$_3$ films on different substrates were studied with ultraviolet photoemission spectroscopy (UPS) and X-ray photoemission spectroscopy (XPS). The research indicates that Au is more suitable for the film growth than the other substrates, especially when the film is very thin. The poor adsorption of the precursors may make it difficult to form MAPbI$_3$ thin film on ITO. Furthermore, it is found that the charge transfer efficiency at the interface between PEDOT and MAPbI$_3$ is relatively high, which indicates that PEDOT can act as an effective hole transport layer for MAPbI$_3$-based devices.

1. Introduction

Organic-metal halide perovskites solar cell (PSCs) have attracted intensive interests in recent years because of the advantages such as: simple structure, easy fabrication, low cost and high efficiency, etc.[1-4]. PSCs have made great achievements in the past decade. The power conversion efficiency (PCE) of MAPbI$_3$-ased solar cells have been improved from 3.8% in 2009 to 25.2% in 2019[5-7]. Although their remarkable conversion efficiencies are almost comparable to that of the traditional silicon solar cells, the research of perovskite solar cells is just mainly focus on the technical level of material synthesis and device preparation. While the relationship between interface electronic structure and the macro device performance is still lack of deep research. The interface electronic structure and the energy level alignment play a crucial role in the open-circuit voltages and the short-circuit currents of the PSCs. Mismatch in energy level structure between adjacent functional layers and electrodes will results in reduced open circuit voltage, short-circuit current and fill factor [4]. Solution process has been widely employed to fabricate perovskite films for the advantages like low cost, high efficiency, etc. But high purity, large area uniform films with ideal stoichiometric ratio can’t be fabricated easily by solution process [8-9]. And also, the film thickness can’t be controlled precisely with solution process, which is essential for the electronic structure research. Vacuum evaporation can get high quality films, especially for the purity, uniformity, and area scalability [10-11]. So, a film prepared by vacuum evaporation is especially suitable for precise investigations for interface electronic structure [12]. Therefore, to explore the working mechanism of the interface and to optimize the solar cell performance, we need to understand the electronic structure and energy level arrangement of the interfaces [13-14]. The growth mechanism of perovskite film on different substrates might be quite different and essential to research the interface electronic structure. Some interface electronic
researches have been performed like MAPbI$_3$ on C$_60$, TiO$_2$ etc [15]. But the theoretical mechanisms are still not quite clear and need to be studied in depth.

In this work, we first optimized the preparation parameters of MAPbI$_3$ films by dual-source vacuum evaporation. Then, the as thin as 20 nm MAPbI$_3$ films were deposited on three representative substrates, which are Au (metal), PEDOT (organic) and ITO (oxide) at the same time to research the substrate-dependent growth. We observed that MAPbI$_3$ grew well on Au substrate, which means that the Au surface had better adsorption rate and reaction efficiency compared to the other two substrates. Only a small amount of perovskite formed on ITO and PEDOT substrates, which indicates low adsorption rate or react efficiency. Our results might be helpful to understand the formation mechanism and the electronic structure of MAPbI$_3$ films on different kinds of substrates.

2. Experimental Section

2.1. Film Fabrication

The MAPbI$_3$ films were deposited on different substrates by thermal co-evaporation (the base pressure is about 4.2×10^{-8} torr). MAI (Sigma-Aldrich, ≥98%) and PbI$_2$ (Sigma-Aldrich, 99.999%) were used as precursors. We first deposited thick MAPbI$_3$ films (typical thickness is 200 nm) on silicon wafer to optimize the fabrication process parameters. Then, Au, PEDOT and ITO substrates were adhered on the same sample holder for the deposition to make sure the films are grown in the same condition. Before being loaded into the chamber, the ITO substrates were cleaned with acetone, deionized water mixed with detergent, deionized water, and isopropyl alcohol for 20 min each. The PEDOT substrate was made by spin-coating poly (3,4-ethylenedioxythiophene) film on ITO. The Au substrate was an Au coated silicon wafer by thermal evaporation. The evaporation rates were measured with a quartz crystal monitor which was calibrated by using surface profiler (DektakXT). The rate of evaporation MAI and PbI$_2$ is kept at about 1.2: 1 because MAI is not easily adsorbed on the substrate compared to PbI$_2$. The thickness of the vapour-deposited MAPbI$_3$ film is about 20 nm according to the quartz crystal monitor although it might not be precise because of the quite different adsorption and reaction efficiency.

2.2. Characterization

The crystallinity of the films was analyzed with X-ray diffraction (XRD, Advance D8) with Cu Kα radiation. Raman and steady-state photoluminescence (PL) measurements were performed in the inVia Qontor system (Renishaw, UK) using a 532 nm laser with spot size less than 1 μm. XPS and UPS measurements were performed in a spectrometer chamber (base pressure: 2.0×10^{-10} mbar) which is equipped with a monochromatic X-ray source (Al Kα, hv = 1486.7 eV) and a UV light source (He I$_{α}$, hv = 21.2 eV)[16]. The binding energies of all XPS and UPS spectra were referenced to the Fermi level (EF) of the analysis chamber[17-18]. All the measurements were performed at room temperature.

3. Results and Discussion

Figure 1(a) shows the schematic diagram of the vacuum thermal co-evaporation deposition device. The as-deposited MAPbI$_3$ films arise gray-black and show extensive uniform. Figure 1(b) shows the XRD pattern of as-deposited MAPbI$_3$ film on silicon wafer (the thickness is about 200 nm). The diffraction peaks of MAPbI$_3$ locate at 14.11°, 28.46° and 31.98° corresponding to the (110), (220) and (310) lattice planes, respectively. It indicates that the as-deposited MAPbI$_3$ film is a tetragonal perovskite structure [9]. The strong (110) and (220) diffraction signals demonstrate the good crystallinity and indicate that a further annealing for high quality MAPbI$_3$ is not required. But consider that the deposition temperatures of PbI$_2$ and MAI were about 285 °C and 93 °C, respectively. The perovskite films were just like being annealed during the thermal co-evaporation. The weak peak located at 2θ=12.7° was also observed and we attribute it to the excessive PbI$_2$ in the film, a small amount of PbI$_2$ in the MAPbI$_3$ film can act as a passivation layer and thus improve the surface properties.[19] The XRD spectra shows the successful preparation of MAPbI$_3$ films.
To investigate the substrate-dependent growth of the MAPbI$_3$ film, we deposited MAPbI$_3$ films with the same parameters on Au, ITO, and PEDOT as shown in Figure 2(a). Figure 2(b) shows the PL spectra of the MAPbI$_3$ film deposited on Au, ITO, and PEDOT. The PL intensity is closely related to the photo-generated carrier efficiency and the carrier recombination, thus can reflect the carrier lifetime and diffusion length [20,21]. We found that the PL intensity of MAPbI$_3$ deposited on PEDOT was very weak, this may be because of the poor adsorption efficiency and thus only a small amount of MAPbI$_3$ formed on the substrate, or the high hole transfer efficiency at the PEDOT/MAPbI$_3$ interface. We prefer to the latter because the MAPbI$_3$ film formed on PEDOT is exactly thicker than that of on ITO. PEDOT is an effective hole-extracting layer, so the generated holes can move through the interface as the HOMO of PEDOT is higher than that of MAPbI$_3$, so the PL intensity is very weak[22]. The intensity of MAPbI$_3$ film on Au substrate is much stronger than that of on ITO substrate, which may be attributed to the generated carrier in the film on Au higher than that of on ITO, implying a better crystallization and film quality on Au substrate or the film thickness on Au is thicker than that of on ITO. And we attribute the relatively weak PL intensity of MAPbI$_3$ film on ITO to the poor adsorption and only a small amount of MAPbI$_3$ film formed on it. The peak centers of the films are shown in Table.1, which corresponds to 757.7 nm, 752 nm, and 713.0 nm. The peak centers of the film on Au and ITO substrates are very close to the previous reports [23], however, the center of the film on PEDOT substrate is lower than the reported value. We consider it might relate to the different fabrication process and some doping effects might be happened at the interface.

Table 1. The location of PL peaks of MAPbI$_3$ deposited on different substrates

| Substrate | Au   | ITO  | PEDOT |
|-----------|------|------|-------|
| Wavelength(nm) | 758.8 | 753.5 | 713.0 |

Figure 2. (a) The schematic view of MAPbI$_3$ film prepared on different substrates. (b) PL spectra of MAPbI$_3$ deposited on different substrates.
Raman spectra of MAPbI$_3$ films deposited on different substrates are shown in Figure 3. Lin et al. reported the Raman spectra of MAPbI$_3$ on Fluorine doped tin oxide (FTO), they found that there were three vibration modes correspond to E$^1_2$ (69 cm$^{-1}$), A$^1_1$ (104 cm$^{-1}$) and A$^2_1$ (140 cm$^{-1}$) [23]. Pérez-Osorio et al. researched the Raman spectra of the MAPbI$_3$ film by using first principles, they pointed out the characteristics of Pb-I stretching, Pb-I-Pb bending and rocking motion. They also determined the complex vibration modes of CH$_3$NH$_3$(MA) cation. [24] As shown in Figure 3, the peaks of the film on Au located at 71, 93.4, and 109 cm$^{-1}$. According to the literature, we assigned the peaks at 93.4 and 109 cm$^{-1}$ to the Pb–I stretching modes with B$_{3g}$ symmetries, which mainly reflect the vibration information about the inorganic components in the material. The peak at 71 cm$^{-1}$ is related to the librational/translational modes of organic cations (MA$^+$) in MAPbI$_3$. The spectrum of the film on ITO and PEDOT are similar to that of on Au except for the shoulder peak at about 124.7 cm$^{-1}$. It should be related to spin modes of organic cations in MAPbI$_3$. The spin mode of MA cations has considerable anharmonicity[24]. we also found that the intensity of the Au is stronger than that of ITO and PEDOT, which may relate to the film growth modes and the film quality.

![Raman spectra](image)

**Figure 3.** Raman spectra of MAPbI$_3$ film deposited on different substrate.

The XPS spectra of MAPbI$_3$ film on different substrates are shown in Figure 4. For better visual effects, all the peaks are normalized to the same height. Figure 4(a) shows the evolution of C 1s peaks of the films, it is obviously that each peak contains two peaks. The peaks centered at about 286.2 eV are considered to be the carbon in the MAPbI$_3$ film, and the other peak centered at about 284.5 eV are considered to be amorphous carbon from air or the decomposition products from the MAPbI$_3$ film considering the poor stability of the film. For the film on Au, the intensity of perovskite C 1s at 286.2 eV is quite stronger than that of at 284.5 eV, on the contrary, for the films on PEDOT and ITO substrates, the intensities of perovskites C 1s are quite weaker than that of at 284.5 eV. This strongly indicated that MAPbI$_3$ film can be more easily formed than that of on PEDOT and ITO, we can infer that only a quite small amount of MAPbI$_3$ film formed on PEDOT and ITO substrates. Consider the existence of C in PEDOT itself, there should be much more MAPbI$_3$ film formed on PEDOT than on ITO. This also demonstrated that it was the charge transfer that caused the extremely weak PL intensity of the film on PEDOT as shown in Figure 2(b). Olthof et al. also investigated the substrate-dependent electronic structure and film formation of MAPbI$_3$ film on different substrates, and that only a small amount of nitrogen was found on the ITO. Perovskite was not formed after 10 nm deposition. CH$_3$NH$_3$I (MAI) and other nitrogen-containing dissociation products were not adsorbed on the substrate.[25] This is quite similar to our results.

Figures 4(b,c,d) shows the core level of N 1s, Pb 4f$_{5/2}$ and I 3d$_{5/2}$, respectively. The peak center of the films are very similar to the previously reports except for the obvious shift of about 0.4 eV toward high binding energy for the film on ITO. Such a shift was also found at C 1s in MAPbI$_3$. We attribute such a shift to the charging effect. As the MAPbI$_3$ film is quite difficult to form on ITO, and the film
we fabricated here is only about 20 nm, we can infer that the MAPbI$_3$ film on ITO might be not continuous and consists of many defects and impurities (such as PbI$_2$ and hydrocarbons) thus decrease the surface conductivity. In fact, the peak intensity of the film on ITO are also quite weak than that of on Au and PEDOT according to the unnormalized data. So, we can conclude that Au is the best substrate for the growth of MAPbI$_3$ film, and ITO is not a good substrate especially for the very thin MAPbI$_3$ film growth. This may be related to the adsorption ability and reaction efficiency between substrate and precursors, which need a further investigation.

Figure 4. XPS spectra of MAPbI$_3$ films on Au, PEDOT and ITO substrates (a) C 1s, (b) N 1s, (c) Pb 4f$_{7/2}$ and (d) I 3d$_{5/2}$.

Figure 5 shows the UPS spectra of MAPbI$_3$ films on Au, PEDOT and ITO substrates. Figure 5 (a) and (b) are the cut off region and the highest occupied molecular orbital (HOMO) region, respectively. The work function (WF) and the HOMO are both calculated by using the linear extrapolation method as introduced in ref[26]. All the spectra were normalized to the same height. As shown in Figure 5(a), the WF of the films deposited on Au and ITO are detected to be 4.69 eV and 4.21 eV, respectively, which are very close to the previous reports.[25,27] The WF of the film deposited on PEDOT is detected to be 4.48 eV, which is slightly lower than the reported value. The measured WF is consistent with the change trend of XPS, with a shift of about 0.4 eV towards high binding energy for the film on ITO compare with that of on Au. As shown in Figure 3 (b), the HOMO of MAPbI$_3$ films deposited on PEDOT and Au corresponds to 1.91 eV and 1.78 eV below the Fermi Level (E$_F$), respectively, a little higher than the previous reports.[4] While the HOMO of the film on ITO is 1.83 eV, which is very close to the previous report.[25] We attribute it to the different fabrication and measurement conditions, in our case, the films are not characterized in-situ, the sample was exposed to air for a few minutes before it was loaded into the measure chamber. The MAPbI$_3$ film is not quite stable in the air and UPS is a surface sensitive measure method, so the UPS data might be deferent compared with that of in-situ characterization results.
Figure 5. UPS spectra of MAPbI$_3$ films on Au, PEDOT and ITO substrates: (a) Cut-off region, (b) HOMO region.

4. Conclusion
In summary, MAPbI$_3$ films were deposited on three representative (Au, PEDOT, ITO) substrates in the same condition with optimized process parameters. PL, XPS, UPS, and Raman measurements were employed to research the formation process of the films on different substrates. The PL intensity and the XPS intensity of the film on Au are quite high than that of on PEDOT and ITO, which indicates that Au is more suitable for the MAPbI$_3$ growth compared with the others. The extremely weak PL intensity of the film on PEDOT indicated a high hole transfer efficiency which indicated that PEDOT can act as an efficient hole transfer layer for MAPbI$_3$. The film is difficult to form on ITO especially at the beginning of the deposition because of the poor adsorption. The results will be useful for the growth research and interface electronic research of MAPbI$_3$ film.

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6. References
[1] G. Hodes. Perovskite-Based Solar Cells. Science, 342(2013)317-318.
[2] Y.F. Liu, C.Y. Xie, W.J. Tan, X.L. Liu, Y.B. Yuan, Q.T. Xie, Y.Z. Li, Y.L. Gao, Analysis of light-induced degradation in inverted perovskite solar cells under short-circuited conditions, Org. Electron. 71 (2019) 123-130.
[3] W.J. Tan, C.Y. Xie, Y.F. Liu, Y. Zhao, L. Li, X.L. Liu, Y.B. Yuan, Y.Z. Li, Y.L. Gao, Initial photochemical stability in perovskite solar cells based on the Cu electrode and the appropriate charge transport layers, Synth. Met. 246 (2018) 101-107
[4] Y. Zou, Q. Meng, H. Mao, D.B. Zhu. Substrate effect on the interfacial electronic structure of thermally-evaporated CH$_3$NH$_3$PbI$_3$ perovskite layer. Organic Electronics 41 (2017) 307-314
[5] A. Kojima, K. Teshima, Y. Shirai, T. Miyasaka, Organometal halide perovskites as visible-light sensitizers for photovoltaic cells, J. Am. Chem. Soc. 131 (2009) 6050–6051
[6] E.H. Jung, N.J. Jeon, E.Y. Park, C.S. Moon, T.J. Shin, T.-Y. Yang, J.H. Noh, J. Seo, Efficient, stable and scalable perovskite solar cells using poly(3-hexylthiophene), Nature 567 (2019) 511-515.
[7] NREL efficiency chart. https://www.nrel.gov/pv/assets/images/ best-research-cell- efficiencies. 20191106.png.
[8] Q. Wang, Y.C. Shao, H.P. Xie, L. Lyu, X.L. Liu, Y. Gao, and J.S. Huang, Qualifying composition dependent p and n self-doping in CH$_3$NH$_3$PbI$_3$, Appl. Phys. Lett. 105, 163508 (2014).
[9] Y.Z. Li, X.M. Xu, C.G. Wang, C.C. Wang, F.Y. Xie, J.L. Yang, Y.L. Gao. Investigation on thermal evaporated CH3NH3Pbl3 thin films, AIP Adv. 5 (2015) 097111.
[10] P. Liu, et al, Interfacial Electronic structure at the CH3NH3Pbl3/MoOx Interface, Appl. Phys. Lett. 106 (2015).
[11] Y. Z. Li, X. M. Xu, C. G. Wang, C. C. Wang, F. Y. Xie, J. L. Yang, Y. L. Gao, Degradation by Exposure of Coevaporated CH3NH3Pbl3 Thin Films. J. Phys. Chem. C 119 (2015) 23996–24002.
[12] Y. Zhao, et al, Fullerene (C60) Interlayer modification on the electronic structure and the film growth of C8-BTBT on SiO2, Synth. Met. 229 (2017) 1-6.
[13] Q.-K. Wang, R.-B. Wang, P.-F. Shen, C. Li, Y.-Q. Li, L.-J. Liu, S. Duhm, J.-X. Tang, Energy Level Offsets at Lead Halide Perovskite/Organic Hybrid Interfaces and Their Impacts on Charge Separation, Adv. Mater. Interfaces 2 (2015) 1400528.
[14] E.S. Thibau, A. Llanos, Z.H. Lu, A simple rule for determining the band offset at CH3NH3Pbl3/organic semiconductor heterojunctions, Appl. Phys. Lett. 108 (2016) 021602.
[15] C.G. Wang, X.L. Liu, C.C. Wang, X.M. Xu, Y.Z. Li, F.Y. Xie, Y.L. Gao, Molecular Orientation of Copper Phthalocyanine (CuPc) Thin Films on Different Monolayers of Fullerene (C60) on SiO2/Highly Oriented Pyrolytic Graphite (HOPG), Applied Physics Letters, 106: 121603 (2015).
[16] S.T. Wang, D.M. Niu, L. Lyu, Y.B. Huang, X.H. Wei, C. Wang, H.P. Xie, Y.L. Gao, Interface electronic structure and morphology of 2,7-dioctyl[1]benzo[3,2-b]benzothiophene (C8-BTBT) on Au film, Appl. Surf. Sci. 416 (2017) 696-703
[17] X.L. Liu, C.G. Wang, C.C. Wang, I. Irfan, Y.L. Gao, Interfacial electronic structures of buffer-modified pentacene/C60-Based charge generation layer, Org. Electron. 17 (2015) 325-333.
[18] S.T. Wang, L. Lyu, D.M. Niu, L. Zhang, H. Huang, Y.L. Gao, Breaking down and reconstruction of islands during the film growth of CuPc on HOPG. Appl. Phys. Lett. 114 (2019) 241602.
[19] T.Y. Zhang, N.J. Guo, G. Li, X.F. Qian, Y.X. Zhao, A controllable fabrication of grain boundary PbI2 nanoplates passivated lead halide perovskites for high performance solar cells. Nano Energy, 26 (2016) 50-56.
[20] W. D. Zhu, L. Kang, T. Yu, B.H. Lv, Y.R.Q. Wang, X.Y. Chen, X.Y. Wang, Y. Zhou, Z.G. Zou, Facile face-down annealing triggered remarkable texture development in CH3NH3Pbl3 films for high-performance perovskite solar cells, ACS Appl. Mater. Interfaces 9 (2017) 6104–6113.
[21] M. Bouzidi, S. Soltani, Z. Chine, A. Rebey, M.K. Shakfa, Time-resolved photoluminescence and photoreflectance spectroscopy of GaN layers grown on SiNtreated sapphire substrate: optical properties evolution at different growth stages, Opt. Mater. 73 (2017) 252–259.
[22] Q. Wang, C.-C Chueh, M. Eslamian, A.-Y. Jen, Modulation of PEDOT:PSS pH for Efficient Inverted Perovskite Solar Cells with Reduced Potential Loss and Enhanced Stability[J]. ACS Appl. Mater. Interfaces 8 (2016) 32068-32076.
[23] S.H. Lin, et al. Enhancement of photo-electrochemical reactions in MAPbI3/Au. Materials Today Energy 9 (2018) 303-310
[24] M. Pérez-Osorio et al. Raman Spectrum of the Organic–Inorganic Halide Perovskite CH3NH3Pbl3 from First Principles and High-Resolution Low-Temperature Raman Measurements. J. Phys. Chem. C. 122(2018) 21703-21717
[25] S. Othof, K. Meierholz, Substrate-dependent electronic structure and film formation of MAPbI3 perovskites. Scientific Reports, 7 (2017) 40267.
[26] Y.Z. Li, X.M. Xu, C.C. Wang, B. Ecker, J.L. Yang, J.S. Huang, Y.L. Gao, Light-induced degradation of CH3NH3Pbl3 hybrid perovskite thin film, J. Phys. Chem. C, 121(2017)3904–3910.
[27] C. Wang, Y. Li, X. Xu, C.G. Wang, F.Y. Xie, Y.L. Gao, Degradation of Co-Evaporated Perovskite Thin Films. MRS Advances, 1(2016) 923-929.