Purely physical fabrication of 10 cm × 10 cm, highly uniform PbI₂ thin films on rigid and flexible substrates for x-ray photodetection application

Cite as: APL Mater. 8, 031108 (2020); https://doi.org/10.1063/1.5145236
Submitted: 16 January 2020 . Accepted: 20 February 2020 . Published Online: 05 March 2020

Hui Sun, Qing Wei, Qianfa Su, Xinghua Zhu, Peihua Wangyang, Xiuying Gao, and Dingyu Yang

Cryogenic probe stations
for accurate, repeatable material measurements
Purely physical fabrication of 10 cm × 10 cm, highly uniform PbI$_2$ thin films on rigid and flexible substrates for x-ray photodetection application

Hui Sun, Qing Wei, Qianfa Su, Xinghua Zhu, Peihua Wangyang, Xiuying Gao, and Dingyu Yang

AFFILIATIONS
1 College of Optoelectronic Engineering, Chengdu University of Information Technology, Chengdu 610225, China
2 School of Intelligent Manufacturing, Sichuan University of Arts and Science, Dazhou 635000, China
3 Author to whom correspondence should be addressed: sunhui@cuit.edu.cn

ABSTRACT
Lead iodide, PbI$_2$, is one of the promising metal halide materials used for x- and γ-ray detection; it is also a key constituent of organometallic halide perovskites for low-cost solar cells. Here, we report a mature technology for the fabrication of microelectronic devices—an electron beam evaporation method to prepare highly uniform PbI$_2$ thin films with a size of up to 10 cm × 10 cm on various rigid and flexible substrates at room temperature; the fabricated x-ray detectors show a consistent detection performance. The detection performance of the PbI$_2$ thin film based flexible detectors demonstrate high robustness and stability under various bending states, suggesting themselves as potential candidates for the development of next-generation, large-area, and flexible x-ray detecting devices by using pure PbI$_2$ films.

© 2020 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/). https://doi.org/10.1063/1.5145236

I. INTRODUCTION

Recently, lead iodide (PbI$_2$) has gained extensive attention due to its prominent application in high efficiency perovskite solar cells (PSCs), such as organometallic halide perovskite materials, including methylammonium (CH$_3$NH$_3^+$, MA) lead iodide (MAPbI$_3$), formamidinium (NH$_2$CH=NH$_2^+$, FA) lead iodide (FAPbI$_3$), and CsPbI$_3$ (an all-inorganic perovskite). These perovskite single crystals and film materials also present huge application potential in x-ray detection and imaging. PbI$_2$ is reported widely for x-ray detection due to its constituents being elements with high atomic numbers, lead (Z = 82) and iodine (Z = 53), which result in a large absorption coefficient and high photon stopping power. In fact, PbI$_2$ crystals are considered unpromising materials for x- and γ-ray photon detection mainly due to their low Young’s modulus (E) (about 17 GPa) [19], small hardness [20], and easy cleavability, posing a great challenge for device fabrication and processing. However, from the perspective of flexible device application, a material with low Young’s modulus is generally perceived as a less stiff material, i.e., it has higher flexibility. This characteristic can endow PbI$_2$ materials with the application potential in flexible electronic devices. Besides, PbI$_2$ polycrystalline films can be strengthened using this mechanical property and can be prepared by using multiple methods, such as chemical vapor deposition or thermal evaporation, atomic layer deposition (ALD), and solution processing, including spin coating, spray coating, and inkjet printing. However, a dramatic structural change during vapor-phase deposition was found with the thermal evaporation method, mainly the strong dependence of grain orientations on substrate temperature and coating materials [tindoped indium oxide (ITO) and gold (Au) coated substrates]. ALD offers the ability to coat large-area films uniformly and a simple means to control film thickness accurately at a low process temperature (below 90°C) [22]. Lots of PbI$_2$ thin-film preparations with solution processing techniques utilize dimethylformamide (DMF),
dimethyl sulfoxide (DMSO), or a mixture of the two solvents, followed by the preparation of a perovskite layer. Usually, the wet liquid film is dried at an atmospheric environment and low temperature (less than 120 °C) in a short time (usually a few minutes) to obtain PbI₂ films. Solution processing is a representative of the low-cost thin film fabrication method. Actually, a diversified PbI₂ thin film preparation process can meet the requirements of different application scenarios, for example, photovoltaic cells, photodetectors, radiation detectors, and 2D devices. As we all know, electron beam evaporation (eBE) is one of the standard and mature technologies for the fabrication of microelectronic devices, in addition to the physical vapor deposition (PVD) method, usually used for metal, dielectric, and organic semiconductor layer deposition. In addition, it is worth mentioning that the low impurity level and extreme versatility belong to the eBE method. Besides, the eBE process is suitable for a high-purity film deposition under low temperature due to the high electron bombarding energy, high evaporation rate, and high kinetic energy of the evaporative particle. Comparatively speaking, the eBE process can provide good controllability and robustness to deposit uniform PbI₂ films on various substrates, such as silicon wafer (Si), electronic glass, polyethylene glycol terephthalate (PET), polyimide (PI), and polyethylene (PE), which is beneficial for the fabrication of multiple devices including solar cells, sensors, and luminescent devices. Moreover, film deposition under room temperature is necessary because the PET and PE substrates are very sensitive to high temperature. Therefore, the deposition of PbI₂ films by eBE offers a helpful solution to fabricate functional devices.

In this work, PbI₂ thin films with a size of up to 10 cm × 10 cm were deposited on rigid and flexible substrates under room temperature (RT) by using the eBE method. According to the characterization of surface morphology, structure, and optical performance, a stable and consistent film structure on different substrate materials endow the as-grown films. Impressive performance under x-ray exposure was obtained from simple devices with as-deposited PbI₂ films. In addition, flexible devices were prepared by depositing PbI₂ films directly on patterned-electrode PET substrates, also demonstrating a sensitive and repeatable response under different bending states.

II. EXPERIMENTAL SECTION

PbI₂ thin films were deposited on rigid and flexible substrates by using the electron beam evaporation method at room temperature with a working pressure from 1.5 × 10⁻⁴ (background vacuum) to 5.2 × 10⁻⁴ Pa and a deposition rate of about 10 nm/s monitored by using a quartz crystal oscillator. For one cycle of deposition, the emission voltage and the emission current are typically −6 kV and 6 mA (±1 mA), respectively, and the time duration is 7 s. After one cycle of deposition, the next cycle will be performed when the pressure recovers to the initial background vacuum. The recovery time depends on the specific vacuum system. Commercial high-purity and ultra-dried PbI₂ (99.999%, 5 N) powder (Kaiyada materials, Hangzhou) was used as the source material. The powder was made into a cylindrical evaporation source through isostatic pressing at room temperature, which can reduce the splash effect during electron beam bombardment. 10 cm × 10 cm polyethylene (PE; ∼15 μm in thickness) and indium tin oxide (ITO) film-coated polyethylene terephthalate (PET; 125 μm) were employed as flexible substrates, and a 4-inch monocrystalline silicon wafer (p-Si; 300 nm SiO₂) and ITO-coated electronic glass were used as rigid substrates. All the substrates were cleaned by ultrasonic oscillation in acetone, ethanol, and deionized water, dried by a high purity nitrogen flow (99.999%), treated by an argon plasma (PEC-6, MTI Corporation), and finally mounted on a customized fixture for film preparation. The substrates basically maintain room temperature during the deposition process without any heat and cooling measures. The film thickness was determined by a KLA Alpha-Step D-600 stylus profiler. The film structure and optical performance were calculated by x-ray diffraction (XRD, Bruker D8) using a UV-vis spectrophotometer (UV-2550, Shimadzu). The surface morphologies of the as-grown thin films were investigated by contact mode atomic force microscopy (AFM, CSPM5500, Being Nano-Instruments Ltd.) in combination with a Gwyddion data analysis tool.

The interdigital electrode was fabricated by using a Nd:YAG fiber laser (1064 nm) engraved in an argon (Ar) atmosphere with a designed CAD drawing file and 10 W output power for ITO layer ablation. The width of the ITO layer and the electrode spacing are both 0.5 mm. PbI₂ thin films were deposited on the patterned electrode area of the rigid and flexible substrates. Finally, polydimethylsiloxane (PDMS, Sylgard 184), serving as the packaging layer, was spin-coated on the active area to prevent moisture and oxidation. Electrical parameters and detector performance were measured by a Keithley 6517B electrometer combining with an integrated tungsten (W) target x-ray source (Optima 97008, Oxford Instrument), while the detectors were placed in an electromagnetic and radiation shielding box. The output (tube voltage, tube current, and expose duration) of the x-ray source was controlled through a Windows based program interface. All the function tests were performed under room temperature and ambient atmosphere.

III. RESULTS AND DISCUSSION

The low melting point (∼406 °C) of PbI₂ crystals indicates a relatively low electron bombarding energy for thin film deposition by using the eBE method, typically an acceleration voltage of −6 kV and an emission current of 5–8 mA at a background vacuum of 1.5 × 10⁻⁴ Pa in our experiment. Generally, the film thickness increases along with the deposition time. However, for PbI₂, a long deposition time will lead to a coarse and loose film, and even the powdered film will result in a lightproof and flimsy film structure. In order to fabricate a translucent and dense film, multiple deposition cycles were performed, with one cycle about 75 nm in thickness. Figures 1(a) and 1(b) show the bright yellow PbI₂ films on various rigid and flexible substrates under ambient light. The film on the Si wafer shows highly reflective characteristics or approximate specular reflection from visibility. Twenty-five samples were cut for uniform evaluation, such as surface morphology, crystallization, thickness, and optical performance, as tagged in Fig. 1(a). AFM reveals a compact film structure for all substrates, as shown in Fig. 1(c). A uniform film morphology appears in the same substrates at different positions, for example, 1#, 7#, 13#, and 19#, in the PbI₂/glass system, as shown in Fig. 1(d). The value of the roughness average of the as-grown PbI₂
FIG. 1. PbI$_2$ thin films deposited by using electron beam evaporation under room temperature: photographs of the films on (a) rigid substrates (electronic glass, 4-in. Si wafer, and ITO-coated glass) and (b) flexible substrates (ITO-PET and PE) and AFM images of the films on (c) various substrates and (d) glass at different positions; scale bar: [(a) and (b)] 10 mm and [(c) and (d)] 100 nm.

The film is from 2.85 nm to 3.05 nm for the entire film area, indicating a nanoscale fine film surface (see Fig. S1a in the supplementary material). Furthermore, the roughness of the film on the Si wafer and the ITO-coated glass is 2.05 nm and 2.30 nm, respectively, less than that on the electronic glass substrate. The analysis of AFM results indicates that the grain size ranges from 80 nm to 200 nm (see Fig. S1b in the supplementary material), although the grains that constitute the whole film were typically granular instead of a regular shape.

Figures 2(a) and 2(b) present the XRD patterns of the as-grown PbI$_2$ thin films on electronic glass, ITO-coated glass, ITO-coated PET, and Si wafer substrates and the different positions on the ITO-coated glass [Fig. 2(b)]. The (001), (002), (003), and (004) diffraction peak indexes correspond to a 2H PbI$_2$ lattice structure (PDF#07-0235), indicating a (001) preferred orientation or a highly textured character. The widened peak at $2\theta = 25.95^\circ$ corresponds to the PET substrate. The full width at half maximum (FWHM) value of the...
Structural characterization of the PbI₂ thin films: (a) XRD patterns of the films on Si, glass, ITO-coated glass, and ITO-coated PET substrates, (b) XRD patterns of the films on ITO-coated glass at different positions (the number refers to Fig. 1(a); inset: enlarged (001) peak), (c) the FWHM value of the (001) peak of the film on ITO-coated glass at different positions and on different substrates, (d) film thickness distribution on ITO-coated glass, (e) film thickness distribution on a 4-in. Si wafer, (f) average thickness of the films on different substrates with the same deposition cycle, and (g) the linear plot of film thickness dependent on the deposition cycle.

(001) diffraction peak of the film deposited on the ITO-coated glass ranges from 0.155° to 0.184°, and the value in the central areas (7#, 9#, 13#, 17#, and 19#) is smaller than that at the edge areas (1#, 21#, and 25#), as shown in Fig. 2(c). Besides, the films on Si and electronic glass present a smaller FWHM value than the ITO-coated glass and PET. A small FWHM value of the diffraction peak implies high crystallinity of the film. The distribution and uniformity of thickness is key to large-area film deposition and further device fabrication. The thickness was determined by using a stylus profiler range from 200 nm (±5 nm) to 208 nm (±5 nm) toward the film on ITO-glass with three deposition cycles, while the maximum deviation is ±2%, as shown in Fig. 2(d). Likewise, a small deviation in thickness is presented mainly in the central area, which agrees with the XRD results. The thickness of the film on the 4-in. Si wafer ranges from 439 nm (±3 nm) to 449 nm (±3 nm) with six deposition cycles, while the deviation is less than 1%, as shown in Fig. 2(e). It is thought that the smaller thickness deviation of the film on the Si wafer can be attributed to the excellent surface structure and the state of the Si substrate. Figure 2(f) shows that the film thickness after three deposition cycles is 228 nm (±10 nm), 206 nm (±8 nm), 220 nm (±3 nm), 210 nm (±10 nm), 215 nm (±10 nm), and 220 nm (±20 nm) for electronic glass, ITO-glass, Si, ITO-PET, PI, and PE substrates, respectively. The thickness difference of the films on various substrates could be due to the difference in the substrate’s surface structure, such as amorphous (glass and ITO-glass), single-crystal (Si wafer), and plastic substrate (PET, PI, and PE). On the other hand, a finer control of the deposition process is necessary to obtain a consistent sample during different batches. Therefore, linear dependency between film thickness and deposition cycle need to be obtained, as shown in Fig. 2(g).

Optical transmittance (wavelength 400 nm–850 nm) reveals the uniformity and consistency of the large-sized film, as shown in Fig. 3(a). About 80% transmittance of the PbI₂ thin film was obtained during the wavelength of visible light. A thin film interference phenomenon is presented from 500 nm to 850 nm with a distinctly constructive and destructive interference of the transmittance curve involving the film thickness of the measuring area. Ideally, all the transmittance curves will overlap each other if the thickness is identical. Therefore, the dispersive transmittance curve, as shown in Fig. 3(a), indicates the deviation in the film thickness, which is in agreement with the results from the stylus profiler. Figure 3(b) shows the statistical distribution of the transmittance of the entire film at 550 nm, 600 nm, and 650 nm. Qualitatively, the peaks and valleys of the curves correspond to 550 nm and 650 nm,
The fabrication process of the PbI$_2$ thin film based x-ray detector on the plastic or glass substrate is presented in Fig. S2 (supplementary material). Interdigitated ITO-film electrodes were patterned by using laser ablation, and the PbI$_2$ thin films were deposited by using eBE. After that, the device was encapsulated with silicone rubber curing at 50°C. The entire process is a chemical free and solution free reaction, leading to high reproducibility and being environmentally friendly. The inset of Fig. 4(a) shows the PbI$_2$ thin film based x-ray detectors on glass and PET substrates. Due to the transparent silicone rubber and ITO electrodes, the bright yellow PbI$_2$ film is also visible. The incident x-ray photons interact with the PbI$_2$ thin film to create electron hole pairs (EHPs), separated under applied field and realizing photoelectric conversion, as schematically shown in Fig. S3 (supplementary material). The PbI$_2$ thin film based x-ray detector is regarded as a photoconductor in the circuit, leading to a reduction in the resistance and an increase in the current under x-ray exposure. Therefore, dark current is one of the critical parameters to assess detection performance. Generally, a low dark current will contribute to gaining a high sensitivity for the detector. We performed the entire electrical measurements at RT and atmospheric environment, while the humidity was regulated at 40%–50% to ensure accuracy of the low current. The dark current from $6.0 \times 10^{-11}$ A to $7.0 \times 10^{-11}$ A (60–70 pA) was obtained from both PbI$_2$/ITO/glass and PbI$_2$/ITO/PET detectors at 50 V bias voltage, stabilizing relatively during the duration, as presented in Fig. 4(a). This value is lower than that of the detector based on
FIG. 4. Electrical performance of the PbI$_2$ thin films based x-ray detectors under x-ray exposure: (a) I–t curves of the devices under a fixed bias voltage without x-ray exposure (inset: photograph of the device with ITO-glass and ITO-PET substrates), I–V curves of the (b) glass and (c) PET substrate detectors with and without x-ray exposure, (d) photocurrent response of both detectors to pulsed x-ray exposure, (e) rising and falling edges of the photocurrent under excited x-ray, and (f) the linear plot of photocurrent vs x-ray source tube current (tube voltage fixed at 60 kV).

The photoelectric performance of the flexible x-ray detectors made by PbI$_2$ thin film on the PET substrate was measured under x-ray exposure and various bending states. Figure 5(a) shows the device structure of the flexible detector that is corresponding to the device of the inset in Fig. 4(a). Figure 5(b) illustrates the current of the PbI$_2$ thin film based x-ray detectors as a function of bias voltage (0–50 V) under the exposure of x-ray radiation (60 kV, 0.3 mA) at different bending states. The current is reduced to about 17.4% at a 20 mm [distance between substrates on both ends, also see the inset of Fig. 5(c)] bending state, which is due to the reduction in the incident x-ray exposure at a highly bending state. Furthermore, no noteworthy reduction and instability is observed from the photocurrent response to pulsed x-ray exposure with the flexible detector undergoing pristine and various bending states, as shown in Fig. 5(c). Compared with the pristine state, the rectangular-wave photocurrent response was still obtained from the device with different bending states. A detailed comparison with other materials for flexible x-ray detector application is listed in Table S1 (supplementary material). These exciting results indicate high robustness and stability of the PbI$_2$ thin film based x-ray detector.
IV. CONCLUSION

To summarize, we have demonstrated the electron beam evaporation method to deposit uniform PbI$_2$ thin films with sizes of up to 10 cm × 10 cm on various rigid and flexible substrates; the fabricated x-ray detectors show a consistent detection performance under x-ray radiation exposure even if at a bending state. The bright yellow PbI$_2$ films with a compact film structure can be obtained for various substrates. The as-grown thin films show a (001) highly preferred orientation character, while the FWHM value of the (001) peak ranges from 0.155° to 0.184°, indicating high crystallinity. For the entire thin film, the maximum thickness deviation is ±2% for the film on ITO-glass and is even less than 1% for the film on the Si wafer, verifying the feasibility to prepare highly uniform PbI$_2$ films on large-area substrates. About 80% transmittance is obtained during the wavelength of visible light, which indicates the optical uniformity of the large-sized film. The PbI$_2$ thin film based x-ray detectors present a low dark current from 60 pA to 70 pA with 50 V bias voltage and a sharp photocurrent response under pulsed x-ray exposure. Moreover, the detection performance of film based flexible x-ray detectors show high robustness and stability under various bending states, suggesting themselves as potential candidates for the development of large-area, flexible x-ray detecting devices based on PbI$_2$ materials.

SUPPLEMENTARY MATERIAL

See the supplementary material for the AFM analysis of the as-grown PbI$_2$ thin film, the schematic diagram of the detector fabrication process, the schematic diagram of the motion of x-ray photo-induced carriers, and comparison with other materials.

ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (NSFC) under Grant No. 11675029 and the Sichuan Science and Technology Research Foundation (Grant Nos. 2016FZ0018 and 2018YJ0513).

DATA AVAILABILITY

The data that supports the findings of this study are available within the article [and its supplementary material].

REFERENCES

1. Z. Chen, B. Turedi, A. Y. Alsalloum, C. Yang, X. Zheng, I. Gereige, A. AlSaggaf, O. F. Mohammed, and O. M. Bakr, ACS Energy Lett. 4(6), 1258–1259 (2019).
2. S. Kim, I. Jeong, C. Park, G. Kang, I. K. Han, W. Kim, and M. Park, Sol. Energy Mater. Sol. Cells 203, 110197 (2019).
3. M. B. Islam, M. Yanagida, Y. Shirai, Y. Nabetani, and K. Miyano, Sol. Energy Mater. Sol. Cells 195, 323–329 (2019).
4. Y. Zou, H.-Y. Wang, Y. Qin, C. Mu, Q. Li, D. Xu, and J.-P. Zhang, Adv. Funct. Mater. 29(7), 1805810 (2019).
5. D. Yao, C. Zhang, N. D. Pham, Y. Zhang, V. T. Tiong, A. Du, Q. Shen, G. J. Wilson, and H. Wang, J. Phys. Chem. Lett. 9(8), 2113–2120 (2018).
6. C. Wu, D. Wang, Y. Zhang, F. Gu, G. Liu, N. Zhu, W. Luo, D. Han, X. Guo, B. Qi, S. Wang, Z. Bian, Z. Chen, and L. Xiao, Adv. Funct. Mater. 29(34), 1902974 (2019).
M. R. Squillante, and G. Entine, Nucl. Instrum. Methods Phys. Res., Sect. A 20
Chem. Eng. 7(1), 3404–3413 (2019).}

J. Chen, J. Xu, C. Zhao, B. Zhang, X. Liu, S. Dai, and J. Yao, ACS Sustainable
Chem. Eng. 7(3), 3404–3413 (2019).

Q. Fu, X. Tang, B. Huang, T. Hu, L. Tan, L. Chen, and Y. Chen, Adv. Sci. 5(3),
1700387 (2018).

A. Swarnkar, A. R. Marshall, E. M. Sanzehira, B. D. Chernomordik, D. T. Moore,
J. A. Christians, T. Chakrabarti, and J. M. Luther, Science 354(6308), 92 (2016).

Y. Wang, T. Zhang, M. Kan, and Y. Zhao, J. Am. Chem. Soc. 140(39), 12345–
12348 (2018).

C. F. J. Lau, X. Deng, J. Zheng, J. Kim, Z. Zhang, M. Zhang, J. Bing, B. Wilkinson,
L. Hu, R. Patterson, S. Huang, and A. Ho-Baillie, J. Mater. Chem. A 6(14), 5580–
5586 (2018).

B. Li, Y. Zhang, L. Fu, T. Yu, S. Zhou, L. Zhang, and L. Yin, Nat. Commun. 9(1),
1076 (2018).

F. Ye, H. Lin, H. Wu, L. Zhu, Z. Huang, D. Ouyang, G. Niu, and W. C. H. Choy,
Adv. Funct. Mater. 29(6), 1806984 (2018).

Y. Han, S. Y. Lee, and N.-G. Park, Nature 550(7674), 87–91 (2017).

P. Yu, W. Zhu, Y. Liu, J. Zhou, B. Liu, H. Xie, Y. Cao, H. Li, X. Wang, K. Liu,
X. Wang, J. Wang, L. Wang, and W. Huang, Adv. Mater. 31(17), 1806562 (2019).

Y. Wang, L. Gan, J. Chen, R. Yang, and T. Zhai, Sci. Bull. 62(24), 1654–1662
(2017).

X. Zhang, Z. Zhang, R. Lin, K. Xu, J. He, and F. Huang, Adv. Electron. Mater.
2(11), 1600291 (2016).

Y. Wang, Y.-Y. Sun, S. Zhang, T.-M. Lu, and J. Shi, Appl. Phys. Lett. 108(1),
013105 (2016).

X.-l. Chen, Q. Lin, J. Ni, D.-k. Zhang, J. Sun, Y. Zhao, and X.-h. Geng, Thin Solid
Films 520(4), 1263–1267 (2011).

S.-M. Park, T. Ikegami, and K. Ehibara, Thin Solid Films 513(1), 90–94 (2006).

A. Dolgonos, T. O. Mason, and K. R. Poeppelmeier, J. Solid State Chem. 240,
43–48 (2016).

C. Lan, R. Dong, Z. Zhou, L. Shu, D. Li, S. Yip, and J. C. Ho, Adv. Mater. 29(39),
1702759 (2017).

X. Liu, T. Xu, X. Li, Z. Zang, X. Peng, G. Wei, W. Zha, and F. Wang, Sol. Energy
Mater. Sol. Cells 187, 249–254 (2018).

Q. Wei, B. Shen, Y. Chen, B. Xu, Y. Xia, J. Yin, and Z. Liu, Mater. Lett. 193,
101–104 (2017).

G. Lin, L. Dai, and H. P. Hsu, Crystals 9(11), 589 (2019).

J. Liu, B. Shabbir, C. Wang, T. Wan, Q. Ou, P. Yu, A. Tadich, X. Jiao, D. Chu,
D. Qi, D. Li, R. Kan, Y. Huang, Y. Dong, J. Jasieniak, Y. Zhang, and Q. Bao, Adv.
Mater. 31(30), 1902124 (2019).