Perovskite-Compatible Electron-Beam-Lithography Process Based on Nonpolar Solvents for Single-Nanowire Devices

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ABSTRACT: Metal halide perovskites (MHPs) have been studied intensely as the active material for optoelectronic devices. Lithography methods for perovskites remain limited because of the solubility of perovskites in polar solvents. Here, we demonstrate an electron-beam-lithography process with a poly(methyl methacrylate) resist based on the nonpolar solvents o-xylene, hexane, and toluene. Features down to 50 nm size are created, and photoluminescence of CsPbBr3 nanowires exhibits no degradation. We fabricate metal contacts to single CsPbBr3 nanowires, which show a strong photoresponsivity of 0.29 A W⁻¹. The presented method is an excellent tool for nanoscale MHP science and technology, allowing for the fabrication of complex nanostructures.

KEYWORDS: CsPbBr3, perovskite, electron-beam lithography, nanowire, patterning

INTRODUCTION

Metal halide perovskites (MHPs) have attracted increased research attention because of their optoelectronic properties, most notably spurred on by the rapid efficiency improvements in solar cells.¹ Optoelectronic devices such as light-emitting diodes,²,³ X-ray scintillators,⁴,⁵ photodetectors⁶−¹⁰ and others based on MHPs have also been realized on nanoscale devices because standard nanofabrication techniques make frequent use of nonpolar solvents, like water and acetone. A lack of lithographic techniques that exclusively use nonpolar solvents is one of the biggest hindrances to the fabrication of nanoscale MHP devices. Without such techniques, the nanostructuring of both MHP-active and contact layers is not possible. Especially for contacts, low-resolution shadow masking techniques are often used.¹⁴ Recently, advancements have been made toward adapting established lithography techniques for use with perovskites. Nanostructured perovskite has been produced via nanoimprint lithography,¹⁵,¹⁶ ultraviolet-light lithography,¹,¹³,¹⁵,¹⁷ and electron-beam lithography (EBL).¹⁸,¹⁹ EBL has been carried out on MHPs commonly using a poly(methyl methacrylate) (PMMA) resist.¹²,¹³,¹⁹−²¹ PMMA itself is suitable because it is readily commercially available in nonpolar solvents like chlorobenzene and anisole and highly soluble in many other nonpolar solvents.²² Zhang et al.¹⁹ and Yang et al.²⁰,²¹ used 1:3 methyl isobutyl ketone/isopropyl alcohol (MIBK/IPA) developer solutions, a developer commonly used for PMMA, despite its polarity and potential to dissolve MHPs. To mitigate the damage to the MHP, Zhang et al. used only a 5 s development time, while Yang et al. dried the developer solution thoroughly enough to not dissolve CsPbBr3, but neither approach was used to fabricate contacts via a lift-off process. In contrast, Lin et al.¹² used a mixture of chlorobenzene and hexane (1:3) to develop and evaporate 90-nm-thick metal contacts. However, we found this method to be inadequate for contacting CsPbBr3 nanowires (NWs) with a metal of sufficient thickness.

Here, we present and characterize an MHP-compatible PMMA process based on the nonpolar solvents o-xylene, hexane, and toluene.²³,²⁴ The o-xylene/hexane-based developer shows a development performance similar to that of the widely accepted 1:3 MIBK/IPA solution and displays the ability to produce line arrays with 250 nm pitch and 50 nm single lines. Additionally, our process does not use chlorinated solvents, making it more environmentally friendly and reducing the risk of unintentional anion-exchange processes that can occur with chlorinated solvents.²⁵,²⁶ Using this process, CsPbBr3 single-
NW (diameter, 150–350 nm; length, 1–10 μm) devices were successfully fabricated in two- and four-probe geometries. The excellent photoresponse of our devices demonstrates the feasibility of our compatible PMMA process for the fabrication and development of MHP nanoelectronic devices.

## RESULTS AND DISCUSSION

A general scheme for PMMA EBL processing is illustrated in Figure 1a. The overall process is standard, and the novelty lies in the developer solution. A PMMA bilayer is deposited via spin-coating, and then the desired pattern is written using an EBL tool. Electron-beam exposure locally increases the solubility of the PMMA film. Development transfers the written pattern to the PMMA resist layer by selectively dissolving exposed PMMA and, for the bilayer, creates an undercut. Metal is then deposited and lifted off by immersion in a remover, which dissolves all PMMA. Both the standard 1:3 MIBK/IPA and 1:3 chlorobenzene/hexane and several o-xylene/hexane mixtures (1:1, 1:2, and 1:0) and the remaining resist height measured with a profilometer. All chemicals were used as-received without further purification. The normalized PMMA height after development was calculated from the known height of the as-deposited resist film and the measured feature depths. This indicates the development quality because a good developer will only dissolve all exposed PMMA, whereas a poor developer will dissolve unexposed areas or fail to fully dissolve the exposed resist. The normalized height for selected times is shown in Figure 1b. The pure o-xylene developer is the most sensitive, allowing for full development even at low doses of 80 μC cm⁻² and short development times of 30 s. However, it is also the least selective because the remaining resist thickness on the sample measures only 360 nm compared to the nominal resist height of 420 nm. For development times longer than 30 s, o-xylene continues to dissolve unexposed PMMA, reducing the overall resist height and pattern fidelity. Both the standard 1:3 MIBK/IPA and the 2:1 o-xylene/hexane solution show very similar development behaviors with a clearing dose of around 240 μC cm⁻² for development times of 90 and 150 s, respectively, and no appreciable loss in the overall resist height.
In contrast, the more diluted 1:1 o-xylene/hexane and 1:3 chlorobenzene/hexane solutions do not achieve full development within the tested dose and time ranges. Figure 1c shows the normalized PMMA height of the 2:1 o-xylene/hexane developer for different development times. Full development can be achieved for development times as low as 30 s at a dose of around 440 μC cm⁻². While the exact combination of clearing dose and development time will also depend on the sample specific parameters (feature size and pitch, substrate material, and resist thickness), the wide process window shown by this solution should make it suitable for many applications.

Figure 2. (a) 250 nm line array, (b) 100 nm single line, and (c) 50 nm single line created with the 2:1 o-xylene/hexane process. (d) Optical and PL image of a CsPbBr₃ NW throughout device fabrication. A focused 5 mW, 395 nm laser was used for excitation. (e) Photoluminescence spectra of a NW throughout device fabrication. Here, an unfocused 485 nm laser spot with a power density of 2.29 mW cm⁻² was used for excitation. The inset shows the SEM image of a transferred CsPbBr₃ NW.

Figure 3. (a–c) SEM images of different single-NW devices manufactured using o-xylene-based EBL. Parts a and c were imaged at a 30° tilt. (d) Dark and light I–V curves of a device. (e) On/off photoresponse of the same device as that in part c at VSD = 5 V.
To test the resolution possible with this developer, line arrays and single lines were deposited. The 2:1 o-xylene/hexane process with a 120 s development time was used, followed by a 3 s dip in pure o-xylene to ensure clean development and enhance the undercut. A 30 nm layer of gold was deposited and lifted off by immersion in toluene at 60 °C. Line arrays with a line width of 250 nm are shown in Figure 2a and were written with a dose of 280 μC cm⁻². Individual lines with widths as small as 50 and 100 nm (Figure 2b,c) could be created with doses of 360 and 400 μC cm⁻², respectively. Line arrays with lower pitch all failed to lift-off correctly because of feature collapse, likely caused by the undercut and o-xylene dip necessary to obtain a clean substrate surface. While it may be possible to create these structures by using O₂ plasma instead of the o-xylene dip to clean the developed surface, this is likely to cause damage to any underlying perovskite. Instead, the resist and metal thicknesses should be optimized for very small feature sizes, but this is beyond the scope of this initial report.

We investigated how the process affected the optical quality of CsPbBr₃ NWs by recording photoluminescence (PL) spectra at each step of the process because PL is sensitive to defects. The optical images acquired with a focused 5 mW, 395 nm laser are shown in Figure 2d, while the spectra acquired with an unfocused 485 nm laser spot with a power density of 2.29 mW cm⁻² are shown in Figure 2e. Only small shifts of about 5 nm in the PL peak position are observed. The PL intensity shows a slight nonsystematic variation, where the changes in the optical quality. This result also indicates that no damage is done to the material by the electron beam at this acceleration voltage and exposure dose. Thus, we conclude that the process does not cause appreciable degradation of the optical quality of the NWs.

Finally, we used the EBL patterning process to create single-NW devices. The 2:1 o-xylene/hexane process with a 120 s development time and a 3 s o-xylene dip was used again. For the contacts, 20 nm Ti and 200 nm Au were evaporated at an angle and under constant rotation to ensure sidewall coverage at the NW contact. Lift-off was carried out by immersion in toluene at 60 °C. Scanning electron microscopy (SEM) images of fabricated devices are shown in Figure 3a–c, and a typical set of dark and light I–V curves is shown in Figure 3d. This device displays nonlinear behavior with a very low dark current of 0.4 pA at V SD = −5 V. Upon illumination with an optical power of P = 16 mW cm⁻² of 395 nm UV light, the current increases to 40 pA at −5 V, which corresponds to a responsivity R = I on/I off = 0.29 A W⁻¹ with an effective NW area of A NW = 8.38 × 10⁻⁹ cm⁻². The on/off photoresponse of the same device at V SD = 5 V is shown in Figure 3e. When the device is turned on, the current stabilizes within 0.4 ms, with the off response being much smaller than the 0.13 s time resolution of the electronics. Multiple cycles of photocurrent measurements for four different devices can be found in Figure S1. The devices show consistent behavior over the measurement period, with some variation settling within the first two measurement cycles. Furthermore, the variation between devices is quite small.

The nonlinear behavior could be caused by Schottky-like contacts or ion migration effects that screen the external electric field. The strong photoreponse observed for our devices indicates that the nonlinear and hysteresis-like I–V behavior is more likely to be caused by ion migration effects than poor nonohmic contacts. This is further supported by the photocurrent saturating at around 10 nA for V SD = ±5 V for all measured devices, indicating a similar resistance. The contacts were nonohmic due to poor contact quality, the device-to-device variation would be expected to be much more significant. A full exploration of the complex electron- and ion-transport dynamics of these devices is beyond the scope of this paper, but we can conclude that our method can be used for the creation of nanoscale MHP electrical devices.

In conclusion, we have presented an EBL process based on non-polar solvents, which are compatible with MHPs. The process has a large process window and can be used to create nanoscale structures. We use metal evaporation and lift-off to create NW devices, but the process should also be compatible with patterning of the MHP itself. Thus, our results allow for complex nanoscale MHP devices based on top-down processing.

### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsanm.2c00188.

Photocurrent I–V sweeps over multiple cycles for additional devices, SEM images of additional devices, and additional experimental details, materials, and methods (PDF)

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#### Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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#### Notes

The authors declare no competing financial interest.
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ABBREVIATIONS

- EBL = electron-beam lithography
- IPA = isopropyl alcohol
- MHP = metal halide perovskite
- MIBK = methyl isobutyl ketone
- NW = nanowire
- PMMA = poly(methyl methacrylate)
- SEM = scanning electron microscopy

REFERENCES

(1) Li, Z.; Klein, T. R.; Kim, D. H.; Yang, M. J.; Berry, J. J.; van Hest, M. F. A. M.; Zhu, K. Scalable fabrication of perovskite solar cells. Nat. Rev. Mater. 2018, 3 (4), 18017.
(2) Zhang, Q.; Zhang, D.; Gu, L.; Tsai, K. H.; Poddar, S.; Fu, Y.; Shu, L.; Fan, Z. Three-Dimensional Perovskite Nanophotonic Wire Array-Based Light-Emitting Diodes with Significantly Improved Efficiency and Stability. ACS Nano 2020, 14 (2), 1577–1585.
(3) Zhang, Q.; Tavakoli, M. M.; Gu, L.; Zhang, D.; Tang, L.; Gao, Y.; Guo, J.; Lin, Y.; Leung, S. F.; Poddar, S.; Fu, Y.; Fan, Z. Efficient metal halide perovskite light-emitting diodes with significantly improved light extraction on nanophotonic substrates. Nat. Commun. 2019, 10 (1), 727.
(4) Heo, J. H.; Shin, D. H.; Park, J. K.; Kim, D. H.; Lee, S. J.; Im, S. H. High-Performance Next-Generation Perovskite Nanocrystal Scintillator for Nondestructive X-Ray Imaging, Adv. Mater. 2020, 32, 1801743.
(5) Zhang, Z.; Dierks, H.; Lamers, N.; Sun, C.; Novakova, K.; Hetherington, C.; Scheblykin, I. G.; Wallentijn, J. Single-Crystalline Perovskite Nanowire Arrays for Stable X-ray Scintillators with Micrometer Spatial Resolution. Adv. Appl. Mater. 2022, 5 (1), 881–889.
(6) Deng, W.; Huang, L.; Xu, X.; Zhang, X.; Jin, X.; Lee, S. T.; Jie, J. Ultrahigh-Responsivity Photodetectors from Perovskite Nanowire Arrays for Sequentially Tunable Spectral Measurement. Nano Lett. 2017, 17 (4), 2482–2489.
(7) Song, J.; Guo, Y.; Li, C.; Liu, J.; Xu, J.; Wang, Y.; Xu, L.; Xue, J.; Dong, Y.; Tian, T.; Sun, H.; Zeng, H. Ultralarge All-Inorganic Perovskite Bulk Single Crystal for High-Performance Visible-Infrared Dual-Modal Photodetectors. Advanced Optical Materials 2017, 5 (12), 1700157.
(8) Yang, T.; Zheng, Y.; Du, Z.; Liu, W.; Yang, Z.; Gao, F.; Wang, L.; Chou, K. C.; Hou, X.; Yang, W. Superior Photodetectors Based on All-Inorganic Perovskite CsPbI3 Nanorods with Ultrafast Response and High Stability. ACS Nano 2018, 12 (2), 1611–1617.
(9) Lee, W.; Lee, J.; Yun, H.; Kim, J.; Park, J.; Choi, C.; Kim, D. C.; Seo, H.; Lee, H.; Yu, J. W.; Lee, W. B.; Kim, D. H. High-Resolution Spin-on-Patterning of Perovskite Thin Films for a Multiplexed Image Sensor Array. Adv. Mater. 2017, 29 (40), 1702902.
(10) Li, Z.; Li, Z.; Shu, Z.; Fang, X. Facet-Dependent, Fast Response, and Broadband Photodetector Based on Highly Stable All-Inorganic CsCu213 Single Crystal with 1D Electronic Structure. Adv. Funct. Mater. 2020, 30 (28), 2002634.
(11) Harwell, J.; Burch, J.; Filouras, A.; Gather, M. C.; Di Falco, A.; Samuel, I. D. Patterning Multicolor Hybrid Perovskite Films via Top-Down Lithography. ACS Nano 2019, 13 (4), 3823–3829.
(12) Lin, C. H.; Cheng, B.; Li, T. Y.; Retamal, J. R. D.; Wei, T. C.; Fu, H. C.; Fang, X.; He, J. H. Orthogonal Lithography for Halide Perovskite Optoelectronic Nanodevices. ACS Nano 2018, 13 (2), 1168–1176.
(13) Lyashenko, D.; Perez, A.; Zakhidov, A. High-resolution patterning of organohalide lead perovskite pixels for photodetectors using orthogonal photolithography. physica status solidi (a) 2017, 214 (1), 1600302.
(14) Sanders, E.; Soffer, Y.; Salzillo, T.; Rosenberg, M.; Bar-Elli, O.; Yaffe, O.; Joselevich, E.; Oron, D. Remanent Polarization and Strong Photoluminescence Modulation by an External Electric Field in Epitaxial CsPbBr3 Nanowires. ACS Nano 2021, 15 (10), 16130–16138.
(15) Bar-On, O.; Brenner, P.; Lemmer, U.; Scheuer, J. Micro Lasers by Scalable Lithography of Metal-Halide Perovskites. Advanced Materials Technologies 2018, 3 (12), 1800212.
(16) Pouradavoud, N.; Wang, S.; Mayer, A.; Hu, T.; Chen, Y.; Marianovich, A.; Kowalsky, W.; Heiderhoff, R.; Scheer, H. C.; Riedl, T. Photonic Nanostructures Patterned by Thermal Nanoimprint Directly into Organo-Metal Halide Perovskites. Adv. Mater. 2017, 29 (12), 1600503.
(17) Daus, A.; Roldan-Carmona, C.; Domanski, K.; Knobelspies, S.; Cantarella, G.; Vogt, C.; Gratzel, M.; Nazeeruddin, M. K.; Troster, G. Metal-Halide Perovskites for Gate Dielectrics in Field-Effect Transistors and Photodetectors Enabled by PMMA Lift-Off Process. Adv. Mater. 2018, 30 (23), 1707412.
(18) Huang, C.; Zhang, C.; Xiao, S.; Wang, Y.; Fan, Y.; Liu, Y.; Zhang, N.; Qiu, G.; Ji, H.; Han, J.; Ge, L.; Kivshar, Y.; Song, Q. Ultrafast control of vortex microasers. Science 2020, 367 (6481), 1018–1021.
(19) Zhang, N.; Sun, W.; Rodrigues, S. P.; Wang, K.; Gu, Z.; Wang, S.; Cai, W.; Xiao, S.; Song, Q. Highly Reproducible Organometallic Halide Perovskite Microstructures based on Top-Down Lithography. Adv. Mater. 2017, 29 (15), 1606205.
(20) Dou, L.; Lai, M.; Kley, C. S.; Yang, Y.; Bischak, C. G.; Zhang, D.; Eaton, S. W.; Ginsberg, N. S.; Limmer, D. T.; Yang, P. Intrinsic anion diffusivity in lead halide perovskites is facilitated by a soft lattice. Proc. Natl. Acad. Sci. U. S. A. 2018, 115 (47), 11929–11934.
(21) Evchuk, I. Y.; Musii, R. I.; Makita, R. G.; Pritskarina, R. E. Solubility of Poly(methyl methacrylate) in Organic Solvents. Russian Journal of Applied Chemistry 2005, 78 (10), 1576–1580.
(22) Polarity Index. https://macro.lsu.edu/howto/solvents/polarity%20index.htm (accessed 2021-09-12).
(23) Miller’s Home Solvent Polarity Table. https://sites.google.com/site/miller00828/in-solvent-polarity-table (accessed 2022-02-22).
(24) Moia, D.; Gelmetti, I.; Calado, P.; Fisher, W.; Stringer, M.; Game, O.; Hu, Y.; Docampo, P.; Lidsey, D.; Palomares, E.; Nelson, J.; Barnes, P. R. Ionic-to-electronic current amplification in hybrid perovskite solar cells: ionically gated transistor-interface circuit model explains hysteresis and impendence of mixed conducting devices. Energy Environ. Sci. 2019, 12 (4), 1296–1308.
(25) Parobek, D.; Dong, Y.; Qiao, T.; Rossi, D.; Son, D. H. Photoinduced Anion Exchange in Cesium Lead Halide Perovskite Nanocrystals. J. Am. Chem. Soc. 2017, 139 (12), 4358–4361.
(26) Zhang, Z.; Yao, K.; Liu, Y.; Jin, C.; Liang, X.; Chen, Q.; Peng, L. M. Quantitative Analysis of Current-Voltage Characteristics of Semiconducting Nanowires: Decoupling of Contact Effects. Adv. Funct. Mater. 2007, 17 (14), 2478–2489.
(27) Moia, D.; Gelmetti, I.; Calado, P.; Fisher, W.; Stringer, M.; Game, O.; Hu, Y.; Docampo, P.; Lidsey, D.; Palomares, E.; Nelson, J.; Barnes, P. R. Ionic-to-electronic current amplification in hybrid perovskite solar cells: ionically gated transistor-interface circuit model explains hysteresis and impendence of mixed conducting devices. Energy Environ. Sci. 2019, 12 (4), 1296–1308.
(28) Zhao, Y.; Liang, C.; Zhang, H.; Li, D.; Tian, D.; Li, G.; Jing, X.; Zhang, W.; Xiao, W.; Liu, Q.; Zhang, F.; He, Z. Anomalous large interface charge in polarity-switchable photovoltaic devices: an indication of mobile ions in organic–inorganic halide perovskites. Energy Environ. Sci. 2015, 8 (4), 1256–1260.
(29) Tress, W.; Marinova, N.; Moehl, T.; Zakeeruddin, S. M.; Nazeeruddin, M. K.; Grätzel, M. Understanding the rate-dependent
J–V hysteresis, slow time component, and aging in CH3NH3PbI3 perovskite solar cells: the role of a compensated electric field. Energy Environ. Sci. 2015, 8 (3), 995–1004.