Heteroepitaxy of Large-Area, Monocrystalline Lead Halide Perovskite Films on Gallium Arsenide

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ABSTRACT: Lead halide perovskite materials have been emerging as promising candidates for high-performance optoelectronic devices. Significant efforts have sought to realize monocrystalline perovskite films on a large scale. Here, we epitaxially grow monocrystalline methylammonium lead tribromide (MAPbBr$_3$) films on lattice-matched gallium arsenide (GaAs) substrates on a centimeter scale. In particular, a solution-processed lead(II) sulfide (PbS) layer provides a lattice-matched and chemical protective interface for the solid−gas reaction to form MAPbBr$_3$ films on GaAs. Structure characterizations identify the crystal orientations in the trilayer MAPbBr$_3$/PbS/GaAs epistucture and confirm the monocrystalline nature of MAPbBr$_3$ on PbS/GaAs. The dynamic evolution of surface morphologies during the growth indicates a two-step epitaxial process. These fundamental understandings and practical growth techniques offer a viable guideline to approach high-quality perovskite films for previously inaccessible applications.

KEYWORDS: lead halide perovskite, epitaxy, single crystal, gallium arsenide, lead sulfide

1. INTRODUCTION
In the past few years, hybrid lead halide perovskites have become promising candidates as new-generation semiconductors for advanced optoelectronic materials and devices, including remarkable developments like high-efficiency solar cells and light-emitting diodes (LEDs). In spite of these achievements, these devices are mostly based on polycrystalline perovskites, and it is imperative to obtain large-area, single-crystalline perovskite films with a high quality on par with traditional semiconductors like silicon (Si) or gallium arsenide (GaAs). Certain accomplishments have been achieved, for example, by growing monocrystalline perovskite films via lattice-matched homoepitaxy or metamorphic heteroepitaxy on uncommon substrates like silicon (Si) or gallium arsenide (GaAs). Other attempts include the growth of perovskite crystals on more common but lattice-mismatched substrates like Si, GaN, quartz, gold, sapphire, mica, etc., via spin coating, inkjet printing, mechanical slicing, space-confined crystallization, chemical vapor deposition, electrodeposition, etc. However, crystal sizes formed on these lattice-mismatched substrates are limited to scales ranging from several micrometers to several millimeters. In a word, existing approaches either require lattice-matched crystals that are not readily available, or utilize lattice-mismatched substrates that constrain the growth of large-area, monocrystalline perovskite films. In other words, the limited availability of large-area, lattice-matched substrates and their associated growth strategies hinder the formation of large-area, monocrystalline perovskite films, which has long been desired for unprecedented device applications.

2. RESULTS AND DISCUSSION
In this work, we report the epitaxial growth of centimeter-scale, monocrystalline methylammonium lead tribromide (CH$_3$NH$_3$PbBr$_3$) perovskite films on lattice-matched GaAs wafers. Coincidentally, cubic-phase MAPbBr$_3$ has a lattice constant (a = 5.91 Å) close to that of zinc-blende GaAs (a = 5.65 Å), making the lattice-matched or metamorphic epitaxy possible. To evaluate this hypothesis, we first attempt to grow MAPbBr$_3$ via conventional chemical vapor deposition (CVD), following the reaction of methylammonium bromide (CH$_3$NH$_3$Br or MABr) and lead(II) bromide (PbBr$_2$) at 350 °C (Figure S1a):

$$\text{CH}_3\text{NH}_3\text{Br(g)} + \text{PbBr}_2(\text{g}) = \text{CH}_3\text{NH}_3\text{PbBr}_3(\text{s})$$

This reaction produces polycrystalline MAPbBr$_3$ on lattice-matched Si (100) substrates (a = 5.43 Å) (Figure S1b), which is expected and in accordance with previous reports.

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However, the same synthesis process results in the formation of lead (Pb) powders on GaAs (100), which makes the direct CVD growth of MAPbBr$_3$ unsuccessful (Figure S1c). This observation is likely to be attributed to more favorable reactions between bromides and GaAs at 350 °C, which is widely applied in the GaAs dry etching process,$^{33,34}$ Since the Ga–Br bond has a higher bonding energy than that of the Pb–Br bond,$^{35}$ the reaction could dissociate PbBr$_2$ to form Pb solids as well as volatile byproducts like gallium(III) bromide (GaBr$_3$) and arsenic tribromide (AsBr$_3$). In fact, many group III and group V halides form volatile gases (for example, boiling points are 201 °C for GaCl$_3$, 130 °C for AsCl$_3$, 173 °C for PBr$_3$, etc.). Therefore, even if the lattice matching requirement is satisfied, such detrimental processes could prevent the direct epitaxy of various halide perovskites on GaAs at elevated temperatures.

To bypass this challenge, we introduce a lead(II) sulfide (PbS) interface layer to ameliorate the epitaxial growth of MAPbBr$_3$ on GaAs (Figure 1). The PbS layer is grown on GaAs via chemical bath deposition (CBD) by the reaction of lead and sulfur ions in the alkaline solution (Figure 1a):

$$\text{Pb}^{2+}(\text{aq}) + S^{2-}(\text{aq}) = \text{PbS(s)}$$

(2)
The alkaline solution helps eliminate the native oxide on GaAs and facilitate the epitaxial process to form monocrystalline PbS (Figure S2). Subsequently, the MAPbBr$_3$ film is formed by the solid−gas reaction between MABr and PbS in the CVD tube at 145 °C (Figure 1b):

$$3\text{CH}_3\text{NH}_3\text{Br}(g) + \text{PbS}(s) = \text{CH}_3\text{NH}_3\text{PbBr}_3(s) + 2\text{CH}_3\text{NH}_2(g) + \text{H}_2\text{S}(g)$$  (3)

Similar reactions were previously employed to form perovskite-based (MAPbI$_3$) nanocrystals or quantum dots but have not been explored to form large-area monocrystalline perovskite films. The introduction of the PbS interlayer is advantageous in multiple aspects: (1) PbS has a face-centered cubic (FCC), rock salt structure almost perfectly lattice-matched ($a = 5.93$ Å) to MAPbBr$_3$ ($a = 5.91$ Å) and GaAs ($a = 5.65$ Å); (2) PbS protects GaAs against detrimental reactions with halides; (3) PbS serves as a Pb source and directly reacts with MABr, reducing the CVD temperature from 350 to 145 °C. Such material choices and process strategies eventually cause the formation of a large-area, monocrystalline MAPbBr$_3$ film on GaAs, which is systematically analyzed subsequently.

Figure 2 presents materials and crystal characterizations for the PbS/GaAs and the MAPbBr$_3$/PbS/GaAs epitaxial structures. Figure 2a, b show that both the PbS and the MAPbBr$_3$ films form uniform coatings on a GaAs (100) wafer sample with a dimension of around 2 × 2 cm$^2$. Flaws in the edge and on the sample surface are mostly due to the uncleaned sample surface and particles in the CBD growth solution and the CVD chamber. In addition, the MAPbBr$_3$ film presents a highly ordered island structure with cube-shaped crystals all oriented along the cleavage directions ([110] and [11̅0]) of GaAs (100) wafers (Figure 2b, bottom). Cross-sectional scanning electron microscopic (SEM) images (Figure 2c) and corresponding energy-dispersive X-ray spectroscopy (EDS) element mappings (Figure 3) indicate that the as-prepared PbS film has a thickness of ~500 nm after ~5 min CBD, and the MAPbBr$_3$ layer is ~200 nm thick after ~8 h CVD. Electron back scatter diffraction (EBSD) mappings (Figure 2d) clearly illustrate that both the PbS and the MAPbBr$_3$ films have monocrystalline characteristics, with a preferential growth in [110] and [100] directions, respectively.
In agreement with EBSD data, out-of-plane X-ray diffraction (XRD) patterns in Figure 2e confirm that the PbS and the MAPbBr₃ films have growth planes of (220) and (100), respectively. After reaction, the MAPbBr₃ film contains minimal traces of sulfur residues with XRD and EDS signals below the background noise level. For comparison, the same procedures to grow PbS and MAPbBr₃ films are performed on Si and glass substrates. As expected, XRD results indicate that these films are polycrystalline on Si and glass (Figure 4). Additionally, the PbS/GaAs and the MAPbBr₃/PbS/GaAs samples are characterized by Rutherford backscattering spectrometry.⁴³ At the channeling condition (under helium ion beams normal to the film plane), the backscattered ion yields for both samples are notably less than the nonchanneling condition (when samples are tilted by 2⁰), suggesting well-ordered crystal planes for these epitaxial films (Figure 5).

Figure 5. Rutherford backscattering spectra (RBS) at channeling (normal incidence) and nonchanneling (2⁰ tilted orientation) conditions for two samples: (a) MAPbBr₃ on PbS/GaAs and (b) PbS on GaAs. The ion source is 2 MeV ⁴⁺He⁺.

Pole figures in Figure 2f further elucidate in-plane orientations for PbS and MAPbBr₃ crystalline films. The (111) pole figure of PbS with two spots separated azimuthally by 180⁰ at a tilt angle of 35⁰, corresponding to the angle between (111) and (220) planes, indicates the in-plane orientation of PbS with respect to GaAs (Figure 2f, top). Additionally, the (211) pole figure of MAPbBr₃ shows four spots separated azimuthally by 90⁰ at a tilt angle of 35⁰, corresponding to the angle between (211) and (100) planes, and eight spots that are divided into two identical rectangular patterns, indicating the 4-fold symmetry of the (100) plane. Moreover, the four spots at 35⁰ and eight spots at 66⁰ are results of (211) and (112) planar reflections.⁴⁵ It is noted that the (211) planes are unique for simple-cubic perovskite MAPbBr₃ and do not present in the rock salt structure of PbS or the zinc-blende GaAs. The (211) patterns of MAPbBr₃ rotate by 45⁰ in plane in relation to GaAs [100] direction, indicating the orientation of the MAPbBr₃ crystal. The clearly distinct spot patterns with a low background noise reveal the high quality of monocrystalline PbS and MAPbBr₃ films. Results of reciprocal space mapping (RSM) analysis are obtained around (300) and (331) points of MAPbBr₃ (Figure 2g). The asymmetric feature suggests the existence of different in-plane strains in different directions. Collectively, these experimental results clearly demonstrate the single crystal feature of the MAPbBr₃ film epitaxially formed on the PbS/GaAs substrate.

Monocrystalline GaAs (100) substrates have been extensively used in optoelectronic industry at affordable costs up to 8 in. in diameter.⁴⁶ Its widespread availability promises the potential to scale up the heteroepitaxy of MAPbBr₃ films. Figure 6a presents a MAPbBr₃/PbS/GaAs sample with a size of 1.5 × 5 cm², in which three different locations are independently examined with SEM and XRD. Here we perform in-plane phi scanning on the (211) plane of the MAPbBr₃ film since it is unique for the simple cubic perovskite structure and will not be interfered by PbS or GaAs. The surface topology and roughness are similar in different regions across the entire sample (Figure 6b), and consistent XRD peaks of the (211) plane during in-plane phi scanning reveal the single-crystal phase forming across the entire sample surface.

Based on the XRD results obtained in Figure 2, we established a 3D atomic scheme to interpret the MAPbBr₃/PbS/GaAs epistucture, illustrated in Figure 7. This illustration is based on crystal orientations deduced by X-ray characterization, and consistent with the perovskite/PbS and PbS/GaAs interfacial structures described in previous reports.⁴⁶,⁴⁷ According to Figure 2d–f, the epitaxial relation is MAPbBr₃ (100) / PbS (110) / GaAs (100), MAPbBr₃ [001] / PbS [001] / GaAs [011], and MAPbBr₃ [010] / PbS [110] / GaAs [011]. Specifically, the PbS layer grows up along its [110] direction on GaAs (100), and in-plane directions [001] and [110] are parallel to GaAs [011] and [011], respectively. This observation is consistent with previous reports.⁴⁷ While there is only an ~5% mismatch between PbS [110] and GaAs [011], the mismatch between PbS [001] and GaAs [011] is as large as ~50%. Therefore, the lattice registry is most likely metamorphic along GaAs [011] and coincident along GaAs [011], forming a structure with 3 PbS and 2 MAPbBr₃, with a mismatch of ~12%. Similar observations are obtained at the MAPbBr₃/PbS heterointerface. The lattice is almost perfectly matched between MAPbBr₃ [001] and PbS [001], but there is an ~50% mismatch between MAPbBr₃ [010] and PbS [110]. Therefore, the coincident growth along PbS [110] creates a structure with 3 PbS and 2 MAPbBr₃, with a mismatch of ~5%. It should be noted, however, the exact atomic configurations at both interfaces are currently unknown and sketches here are speculative. Detailed structures at the interfaces, including dislocations, film strains, defects, etc., can be further analyzed experimentally and theoretically, using XRD peak shift, confocal spectroscopy, and first-principle simulations in the future. Mechanisms for such a growth preference remain unclear, which are probably ascribed to the different crystal structures of GaAs (zinc blende), PbS (rock salt), and MAPbBr₃ (perovskite).

The epitaxial process for MAPbBr₃ on PbS/GaAs is further investigated by examining the film morphology with SEM and atomic force microscopy (AFM), at different time courses during the growth (Figure 8). The as-grown PbS/GaAs sample
has a root-mean-square (RMS) roughness of $\sim$5.4 nm (Figure 8a). Observed surface defects are likely related to misfit dislocations. Clearly, the growth of MAPbBr$_3$ on PbS/GaAs divides into two distinct steps. In the first step, the solid–gas reaction of MABr and PbS occurs on the PbS surface. The reaction is similar to a previous work reporting the transformation of a PbS polycrystalline film to a polycrystalline perovskite (MAPbI$_3$) layer. After CVD growth for 0.2 h, a
MAPbBr₃ film appears and forms an undulating surface with a period of ~70 nm and an RMS roughness of ~8.5 nm (Figure 8b). In particular, the striped structures follow the cleavage directions of GaAs (100) wafers, which are [110] and [110]. Such an anisotropic growth can be explained by the lattice matching conditions between MAPbBr₃ and PbS, which results in distinct appearance along the two in-plane directions [001] and [010] for MAPbBr₃ (Figure 7). The mechanisms are analogous to the classical Frank–van der Merwe growth in the MAPbBr₃ [001] direction, and the Volmer–Weber growth in the MAPbBr₃ [010] direction. As the process continues, the MABr gas has to diffuse through the MAPbBr₃ film and reacts with the PbS underneath it. The second step forms more rectangular or cubic-shaped MAPbBr₃ crystals and eventually results in a continuous film surface with terrace morphology (Figure 8c, d). After CVD growth for 8 h, the MAPbBr₃ film has an RMS roughness of ~12.6 nm. The maximum roughness (Rmax) is approximately 100 nm and roughness curve is shown in Figure S3. It is noted that the MAPbBr₃ growth rate considerably decreases as the film becomes thicker, since the film growth is eventually limited by the diffusion of MABr gas into the MAPbBr₃ film. We do not observe a thickness increase for the MAPbBr₃ film from 8 to 24 h. During this period, the PbS single-crystal film serves as a lattice-anchored substrate. Such growth kinetics are analogous to the thermal oxidation of silicon.

3. CONCLUSION

In summary, we demonstrate the hetero epitaxy of centimeter-scale, monocrystalline MAPbBr₃ films on GaAs (100) via the gas–solid reaction, with a solution-processed PbS interfacial layer. Such a growth strategy overcomes the limitations of previously explored methods, and heterogeneously integrates an emerging lead halide perovskite material with a traditional III–V compound semiconductor, in a single-crystal format. The applied CBD and CVD processes, as well as the use of GaAs (100) wafers, are compatible with large-scale manufacturing. It is envisioned that these concepts could immediately realize high-quality monocrystalline perovskites on 6 in. and even 8 in. GaAs wafers. Future possibilities involve the large-area production of many other halide perovskites with similar lattice structures, for example, MAPbCl₃ (a = 5.67 Å), CsPbCl₃ (a = 5.61 Å), and CsPbBr₃ (a = 5.87 Å). These monocrystalline materials could potentially produce perovskite-based optoelectronic devices with higher performance, although additional issues associated with design and fabrication must be considered. Preliminary photoluminescence tests show that the monocrystalline MAPbBr₃/PbS/GaAs structure shows a lower PL peak intensity than the polycrystalline MAPbBr₃/PbS/glass sample (Figure S4), mainly due to the high-index and absorptive GaAs substrate. In addition, the band alignments and electron/photon couple at the interfaces in the perovskite/PbS/GaAs trilayer structure should be systematically investigated, which require additional efforts in the future. Furthermore, structure and performance stability is also a critical issue for halide perovskites, and additional coatings could be applied and optimized on the MAPbBr₃ surface to mitigate its degradation with moisture. Collectively, the concepts provide a promising direction for fundamental materials research and advanced device applications.

4. EXPERIMENTAL METHODS

**PbS Growth.** PbS films are grown on GaAs (100) wafers (single-side polished, updoped, AXT Inc.) via chemical bath deposition (CBD) at 50 °C in ambient environment (Figure 1a). The GaAs substrates are cleaved into rectangular pieces with a diamond pen. The chemical solution contains 270 mM sodium hydroxide (NaOH powder, 97%, Alfa Aesar), 10 mM lead nitrate (Pb(NO₃)₂ powder, 99.99%, Aladdin) and 50 mM thiourea (SC(NH₂)₂ powder, 99%, Sigma-Aldrich). The growth rate is ~1 nm/s. The polished side of GaAs faces down in the solution, to avoid PbS cluster particles randomly falling on the growth surface. The PbS deposition is also performed on Si (100) wafers and glass substrates for comparison.

**MAPbBr₃ Growth on PbS/GaAs.** MAPbBr₃ films are formed on PbS/GaAs substrates via chemical vapor deposition (CVD) with a solid–gas reaction (Figure 1b). As-grown PbS/GaAs samples and excessive (~1 g) methylammonium hydrobromide (MABr powder, 98%, TCI Chemicals) are placed inside a quartz tube furnace (OTF-1200X-S, tube diameter 50 mm, MTI Corp.) The reaction of MABr and PbS to form MAPbBr₃ occurs at 145 °C in an argon environment at a pressure of ~100 Pa. The MAPbBr₃ growth rate is also performed on PbS/Si and PbS/glass substrates for comparison.

**MAPbBr₃ Growth on Si and GaAs.** MAPbBr₃ growth is also attempted on Si and GaAs substrates via traditional CVD methods without the PbS interlayer (Figure 1a). Excessive lead bromide (PbBr₂ powder, 99%, TCI Chemicals) and MABr powders are placed into the furnace at 350 °C in the upper stream of Ar flow (30 sccm, 100 Pa), while Si (100) or GaAs (100) wafers are placed in the down stream. The process lasts for ~20 min.

**Materials Characterizations.** X-ray diffraction (XRD) patterns are obtained with a Rigaku S2 diffractometer (40 kV, 40 mA). The PbS/GaAs substrates are plotted with the scanning mode on a Bruker D8 Discover. Samples are placed with the GaAs cleavage direction (110) parallel to one side of the stage. SEM images are taken with a Zeiss GeminiSEM 500 (15 kV), and EBSD data are measured with a Zeiss Merlin. The EDS element mapping uses a sample prepared by a focused ion beam, milled, and transferred on a conductive bracket (electron voltage 15 kV). AFM images are obtained with a BRUKER Multimode 8 (peak-force tapping mode). Rutherford backscattering spectrometry (RBS) and channeling measurements are carried out using a 2 MeV ⁴He⁺ beam from an accelerator at Peking University. Atomic structures were established with Materials Studio 8.0 (Accelrys).

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**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.2c15243.

MAPbBr₃ growth process via conventional CVD on Si and GaAs; cross-sectional HRTEM image; AFM data; and PL spectra (PDF)

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Notes

The authors declare no competing financial interest.

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REFERENCES


Supporting Information

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Additional experimental details, materials, and methods (Supplementary Figures S1–S4)
Figure S1. (a) MAPbBr₃ growth via conventional CVD, by reacting MABr and PbBr₂ on Si or GaAs at 400 °C in argon environment. (b) XRD pattern for the CVD deposited film on Si, indicating the formation of polycrystalline MAPbBr₃. (c) XRD pattern for the CVD deposited film on GaAs, indicating the formation of polycrystalline PbBr₂ and Pb, but no MAPbBr₃. Powder Diffraction Files (PDF) of CsPbBr₃ and PbBr₂ are provided for comparison.
Figure S2

Figure S2. Cross-sectional high-resolution transmission electron microscopic (HRTEM) of the PbS/GaAs interface.
Figure S3. (a) AFM of the MAPbBr$_3$ film grown on PbS/GaAs for 8 hours, (b) 1D scan showing the maximum roughness.
Figure S4. Photoluminescence spectra for MAPbBr$_3$ films grown on PbS/GaAs (red) and PbS/glass (blue). The excitation source is a 365 nm LED.