Pulsed Laser Deposition of Cs$_2$AgBiBr$_6$: from Mechanochemically Synthesized Powders to Dry, Single-Step Deposition

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ABSTRACT: Cs$_2$AgBiBr$_6$ has been proposed as a promising lead-free and stable double perovskite alternative to hybrid and lead-based perovskites. However, the low solubility of precursors during wet synthesis, or the distinct volatility of components during evaporation, results in complex multistep synthesis approaches, hampering the widespread employment of Cs$_2$AgBiBr$_6$ films. Here, we present pulsed laser deposition of Cs$_2$AgBiBr$_6$ films as a dry, single-step and single-source deposition approach for high-quality film formation. Cs$_2$AgBiBr$_6$ powders were prepared by mechanochemical synthesis and pressed into a solid target maintaining phase purity. Controlled laser ablation of the double perovskite target in vacuum and a substrate temperature of 200 °C results in the formation of highly crystalline Cs$_2$AgBiBr$_6$ films. We discuss the importance of deposition pressure to achieve stoichiometric transfer and of substrate temperature during PLD growth to obtain high-quality Cs$_2$AgBiBr$_6$ films with grain sizes > 200 nm. This work demonstrates the potential of PLD, an established technique in the semiconductor industry, to deposit complex halide perovskite materials while being compatible with optoelectronic device fabrication, such as UV and X-ray detectors.

I. INTRODUCTION

Double halide perovskites, of the form A$_2$M’M”X$_6$, have emerged as promising alternatives to hybrid and lead-based perovskites due to their stability and promising optoelectronic properties for photo- and X-ray detectors, light-emitting diodes (LEDs), and wide-band-gap solar cells. This double perovskite structure has opened opportunities to explore a broad composition space, for example, the computational chemistry side of perovskite materials with an estimated 9520 combinations of halide double perovskites, many of them remain unsynthesized. Out of these many possible combinations, Cs$_2$AgBiBr$_6$ stands out as the most widely studied and archetypical double perovskite. As such, many groups have been looking into derivatives of the Cs$_2$AgBiBr$_6$ compound or doping to tune its properties for use as possible photovoltaic (PV) absorbers, light emitters, or photodetectors.

The synthesis of these multicomponent materials (usually containing four or more elements) in the thin-film form has proven to be challenging. Most reports on double perovskites have focused on nanocrystals or solution-based processes where powders are obtained through a filtering and drying process. Specifically for Cs$_2$AgBiBr$_6$, only few studies have shown thin films of double perovskites formed through the traditional spin-coating process, where low solubility of precursors hampered the synthesis of dense, thick films. In this respect, dry, vapor-based processes are preferred for Cs$_2$AgBiBr$_6$. Sequential evaporation, coevaporation, and single-source evaporation have been employed to deposit Cs$_2$AgBiBr$_6$ films; however, postannealing processes are required to achieve or improve the phase purity.

In this work, we demonstrate that pulsed laser deposition (PLD) allows for the single-source, near-stoichiometric deposition of Cs$_2$AgBiBr$_6$ films from powders to pellets to films. We discuss the importance of deposition pressure to achieve stoichiometric transfer and of substrate temperature during PLD growth to obtain high-quality Cs$_2$AgBiBr$_6$ films with grain sizes > 200 nm. This work demonstrates the potential of PLD, an established technique in the semiconductor industry, to deposit complex halide perovskite materials while being compatible with optoelectronic device fabrication, such as UV and X-ray detectors.

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transfer from a solid Cs$_2$AgBiBr$_6$ target to Cs$_2$AgBiBr$_6$ films. This is possible due to a nonequilibrium ablation of the solid target with an excimer laser$^{21}$ and after careful tuning of deposition parameters. In particular, PLD shows extensive promise in photodetector and laser diode applications where highly controlled and highly crystalline (at times epitaxial) growths are required. Below we describe the importance of the PLD optimization process, with a focus on the effect of pressure and substrate temperature to achieve both, near-stoichiometric transfer of Cs$_2$AgBiBr$_6$-pressed powders into thin films and high film crystallinity in a single-step process.

II. METHODS

Cs$_2$AgBiBr$_6$ powders were first synthesized by mechanochemical grinding (i.e., ball milling)$^{22}$ of stoichiometric ratios of CsBr, AgBr, and BiBr$_3$ powders purchased from TCI, Alfa Aesar, and Sigma-Aldrich, respectively. These powders were then pressed uniaxially with a pressure of ~600 MPa for 30 min to form a thick, disc-shaped target, 20 mm in diameter. The deposition of thin films by PLD was performed using a Coherent KrF excimer laser ($\lambda = 248$ nm) to ablate the solid target under vacuum in an Ar atmosphere (various working pressures described in Section III). The ablation took the form of a 4 × 4 mm$^2$ scan, with subsequent ablations (for more thin-film depositions) done on “fresh,” unablated parts of the pressed target. Pre- and postablation analyses of the target via energy-dispersive X-ray spectroscopy (EDX) (Figure S1) indicate no change of the target composition after ablation. As ablation spots are only few micrometers in depth, to reuse the target, the top surface is ground down using a fine sandpaper. This allows for multiple depositions from a single pellet. A target-to-substrate distance of 60 mm was used and the substrate temperature was varied between room temperature (RT) and 200 °C. For all samples, unless otherwise stated, a laser fluence of 0.45 J/cm$^2$, frequency of 8 Hz, and 1 mm$^2$ spot size were used, which led to deposition rates of ~4.3 nm/min. Silicon (100) substrates with a native oxide layer were used to characterize films by X-ray diffraction (XRD), while fused-silica substrates were used for optical analysis. XRD measurements were done in a symmetric configuration using a PANalytical X’Pert PRO with a Cu anode X-ray source. A Perkin Elmer UV–vis–NIR spectrophotometer was used to measure absorbance. The photoluminescence (PL) measurement was excited with a 442 nm laser (Renishaw inVia Reflex micro spectrometer). The response calibration was applied during the measurement to reveal the real shape of the luminescence spectra. Photothermal deflection spectroscopy (PDS) was used to measure the optical absorption of thin films with high sensitivity at a broad spectral range of 400–1000 nm. The deflection of a probe laser beam directly determines the quantity of absorbed light via sample thermal changes.

III. RESULTS AND DISCUSSION

III.I. Mechanochemical Synthesis of Cs$_2$AgBiBr$_6$ Powders and Solid Pellets. CsBr, AgBr, and BiBr$_3$ powders were mixed in 2:1:1 molar ratios. The estimated mass fractions of different phases formed at each stage (derived from Rietveld refinements of powder XRD data; see Figure S2) are presented in Figure 1a.

As seen in Figure 1a, binary precursors react very rapidly in the first few minutes. Nevertheless, the significant fraction of two different Cs–Bi– Br phases, namely, Cs$_3$BiBr$_6$ and Cs$_3$Bi$_2$Br$_9$, at $t < 15$ min, as well as the remaining AgBr (estimated residual mass fraction of 2.7% after 1 h of milling), suggests that the reaction proceeds preferentially in several steps, with an initial reaction between CsBr and BiBr$_3$, followed by the slower incorporation of AgBr. A plausible reaction mechanism based on this data is as follows

$$3 \text{CsBr} + \text{BiBr}_3 \rightarrow \text{Cs}_3\text{BiBr}_6$$  \hspace{1cm} (1)

$$\text{Cs}_3\text{BiBr}_6 + \text{BiBr}_3 \rightarrow \text{Cs}_3\text{Bi}_2\text{Br}_9$$  \hspace{1cm} (2)

$$\text{Cs}_3\text{Bi}_2\text{Br}_9 + 2 \text{AgBr} + \text{CsBr} \rightarrow 2 \text{Cs}_2\text{AgBiBr}_6$$  \hspace{1cm} (3)

To completely elucidate different and potentially complex reaction mechanisms at play, a more detailed analysis at shorter time intervals ($t < 2$ min) would certainly be needed, but this is beyond the scope of this work. On the contrary, it is worth noting that at a relatively short milling time of 15 min the sample consists of nearly phase-pure Cs$_2$AgBiBr$_6$ and remains so after milling for longer times up to 1 h. Optical absorption measurements (Figure 1b) confirm the reaction kinetics observed by XRD. Indeed, the starting powder is transparent below 2.6 eV, which is in line with the reported band gaps of AgBr and BiBr$_3$ (that of CsBr being wider).$^{23,24}$ Upon milling, the absorption red-shifts until reaching a stable onset around 1.95 eV, in accordance with the reported values for Cs$_2$AgBiBr$_6$. For intermediate ball-milling times ($t = 2$ and 5 min), the absorption onset is found within 2.3 and 2.1 eV. While it is tempting to attribute this to the aforementioned intermediate species Cs$_3$BiBr$_6$ and Cs$_3$Bi$_2$Br$_9$, these are actually reported to have wider band gaps.$^{26−28}$ Hence, it is more reasonable to ascribe this absorption to the already-present fraction of Cs$_2$AgBiBr$_6$ at these intermediate times (40–60% in mass approximately; see Figure 1a). Indeed, band gap values ranging from 1.9 to 2.2 eV have been reported for this material.$^{4,29}$ Furthermore, this is also known to vary with structural (dis)order, which could be affected by ball milling.$^{29,30}$ Figure 1c displays the XRD pattern of mechanochemically synthesized Cs$_2$AgBiBr$_6$ powders and the corresponding solid target. Both patterns follow the Cs$_2$AgBiBr$_6$ reference (ICSD 18989), indicating no degradation of the phase after uniaxial pressing.
III.II. Pulsed Laser Deposition of Cs$_2$AgBiBr$_6$ Films from Cs$_2$AgBiBr$_6$ Solid Pellets. One of the known advantages of PLD is the possibility to achieve near-stoichiometric transfer of multicomponent materials. However, this requires careful optimization of parameters such as pressure, laser fluence, and target-to-substrate distance. Based on previous reports, a laser fluence of 0.45 J/cm$^2$ and a substrate to target distance of 60 mm were selected. The effects of pressure and substrate temperature on the stoichiometric transfer and high-crystalline quality are described below.

III.II.I. Effect of Deposition Pressure. During PLD, the plume shape and energetics of the ablated particles arriving at the substrate are strongly influenced by the deposition pressure. At low pressures, the ablated species experience little scattering, arriving at the surface of the substrate with a large portion of their initial kinetic energy. In this way, sputtering of the surface may occur, often preferentially. At higher pressures, more scattering ensues and ablated species are thermalized (i.e., their kinetic energy resembles that of the background gas). To investigate the influence of deposition pressure during PLD from a Cs$_2$AgBiBr$_6$ target, we have grown films at different pressures, tuned via the introduction of Ar gas in the chamber. Figure 2a displays the XRD patterns of films grown at 3, 5.2, and 1.5 mbar pressure. While the (222) plane of Cs$_2$AgBiBr$_6$ is visible at all deposition pressures, EDX indicates excesses of Ag in the film deposited at 1.7 × 10$^{-3}$ mbar. Only at a deposition pressure of 1.5 × 10$^{-1}$ mbar was the growth of a distinct Cs$_2$AgBiBr$_6$ phase observed. SEM cross sections of samples deposited at (b) 1.5 × 10$^{-1}$ and (c) 1.7 × 10$^{-3}$ mbar show the transition from dense (low deposition pressure) to porous (high deposition pressure). The closed red circles note growth conditions used where phase-pure growth was not observed. The star, at 1.5 × 10$^{-1}$ mbar, denotes the nearly phase-pure growth of Cs$_2$AgBiBr$_6$ films.

The link between deposition pressure, thermalization, and stoichiometric transfer can be described following a model proposed by Westwood and summarized in the Supporting Information. Following this model, the distance required for each ablated species to thermalize as a function of the deposition pressure can be estimated. Figure 3 shows the resulting estimates (solid lines) for the elements Cs, Ag, Bi, and Br. The red circles denote experimental points (i.e., films grown at specific deposition pressures) at which no phase-pure growth was observed, while stars denote single-phase growth. Only once the estimated thermalization point of all constituent elements is breached a single-phase growth is observed. As noted, films were grown at 1.5 mbar showed no phase-pure growth while being well above the estimated thermalization region. One possible explanation is that at very high pressures, preferential scattering of lighter atoms occurs affecting the final stoichiometry of the film. Based on this analysis and the results presented in Figure 2, we propose an ideal pressure range between 0.1 and 1 mbar for thermalization of the Cs–Ag–Bi–Br species and near-stoichiometric transfer from the target to the film to occur. Note that this conclusion might vary with materials and specific PLD parameters used.

One strategy to alleviate the pressure-dependence of these growths is through the introduction of excess elements (usually the most volatile) in the source material, as has been shown for other single-source processes and/or materials deposited by either PLD or evaporation.
III.II. Effect of Substrate Temperature. As observed in Figure 2, room-temperature depositions of Cs₂AgBiBr₆ result in porous films, and therefore, to improve the films morphology, the effect of substrate temperature was evaluated. The XRD patterns of room temperature versus 200 °C growths are shown in Figure 4a, with the drastic increase in crystallinity noticeable in the shrinking XRD peak width (inset of Figure 4a) for films grown at 200 °C, and by cross-sectional SEM images (Figure 4b–e). The composition of the films was verified by EDX, showing mean atomic percentages of 21% Cs, 11% Ag, 9% Bi, and 59% Br (statistics in Table S6). The statistical mean shows a near-stoichiometric thin film with a possible bismuth deficiency but remains within a range of error of EDX measurements.

The improved film density and crystalline growth with increased substrate temperature can be described with the Thornton model, a model typically employed for physical vapor deposition of inorganic materials. This model describes the transition in crystallization regimes as a function of its background gas pressure and substrate temperature. At low temperatures, surface diffusion is limited, and the growth is dominated by shadowing effects, introducing porosity into the system (Figure 4b). As the temperature is increased, the added energy allows for surface diffusion to take over. However, atoms are unlikely to diffuse between crystallites and with growth limited to the surface, columnar-like structures are formed (Figure 4c). Finally, at even higher temperatures, bulk recrystallization processes gain enough energy to occur, coalescing the crystallites during the growth to form large grains (Figure 4d). For the growth of Cs₂AgBiBr₆ at 1.5 × 10⁻¹ mbar, these transitions correspond to room temperature, 100 °C, and 200 °C growths, as shown in Figure 4b–e. Unique to PLD, we note that the laser fluence can also be tuned to transition from porous to dense films, respectively (Figure S7), but we refrain from using high values of fluence (1.61 J/cm²) due to possible damage to the target during ablation.

Once the growth was optimized, we verified the optical properties of ~200 nm thick films, grown at 200 °C, through absorbance, PL, and PDS (Figure 5a,b). Notably, we report a 2.24 eV direct band gap through a Tauc plot interpretation of the PDS data (Figure 5a), correlating well with values reported in literature. Longo et al. reported a 2.25 eV direct band gap for sequentially evaporated thin films, and Slavney et al. reported a 2.21 eV direct band gap for single crystals. PDS data also reveals a large density of subgap states, characteristic of Cs₂AgBiBr₆ and linked to nonradiative recombination in Cs₂AgBiBr₆ solar cell devices. The PL peak, centered at 1.90 eV (653 nm), correlates well with reported values of 1.87 and 2.07 eV from single crystals and thin films, respectively. Moreover, we observe a large Stokes shift between the main absorption edge and the PL emission. This effect has been widely reported in literature for Cs₂AgBiBr₆ films. Its origin is debated and assigned to either a tightly bound exciton or to a transition between Bi³⁺ electronic orbitals.

Additionally, it is important to mention that the optimized PLD grown Cs₂AgBiBr₆ films, with no capping layer, were stored in a nitrogen glovebox and showed no sign of degradation, presenting the characteristic PL peak (Figure 5b) even after 1 year. Finally, the stability of the Cs₂AgBiBr₆ target used in this work was analyzed and showed little to no sign of degradation over 1 full year (Figure S8).
IV. CONCLUSIONS

We have demonstrated the dry, single-step deposition of Cs$_2$AgBiBr$_6$ thin films by PLD, starting from a stoichiometric mixture of precursor powders, which were subsequently mechanochemically synthesized and pressed into solid targets with the Cs$_2$AgBiBr$_6$ phase. We demonstrate that tuning the deposition pressure and temperature allows for the fabrication of highly crystalline films of Cs$_2$AgBiBr$_6$. Films deposited at 200 °C show the formation of large crystalline grains with the Cs$_2$AgBiBr$_6$ phase. We demonstrate that the PLD technique can be used to deposit halide perovskite films with complex stoichiometries for a wide range of applications from light-emitting diodes, PV absorbers, UV, and X-ray detectors.

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