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Phys. Status Solidi B, 1–3 (2016) / **DOI** 10.1002/pssb.201600234

physica status solidi b
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basic solid state physics

Hexagonal boron nitride as a cationic diffusion barrier to form a graded band gap perovskite heterostructure

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Received 15 April 2016, revised 6 September 2016, accepted 9 September 2016
Published online 28 September 2016

Keywords 2D materials, cationic diffusion barrier, graded bandgap, hexagonal boron nitride (h-BN), perovskites

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We demonstrate a new technique to produce graded bandgap organohalide perovskite heterostructures using hexagonal boron nitride (h-BN) as a cationic separator. With this technique, we successfully deposit $CH_3NH_3PbI_{3-x}Br_x$ on $CH_3NH_3SnI_3$ without cation mixing.

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1 Introduction Extensive research has been conducted to find economical, low-environmental-impact life-cycle solar cells with high power conversion efficiencies (PCE). Organic–inorganic halide perovskite materials have gained enormous prominence over the past several years. Their long diffusion length and high absorption coefficient makes them an ideal candidate for solar cell technologies [1–5]. Moreover, their tunable band gap properties can allow novel solar cell architectures. The graded band gap solar cell provides an attractive architecture to harvest a broader spectrum of solar radiation. However, therefore there has been no convenient method for forming graded band gap organohalide perovskite materials.

Here we report a technique to produce a graded band gap organic–inorganic halide perovskite heterostructure using hexagonal boron nitride (h-BN) as a cationic diffusion barrier. We sandwich h-BN between two perovskite thin films, $CH_3NH_3SnI_3$ and $CH_3NH_3PbI_{3-x}Br_x$. In this architecture, h-BN plays a very important role to prevent undesirable cation mixing and helps to form a graded band gap. This architecture not only provides a surprisingly robust and time-stable graded band gap perovskite heterostructure, but also yields a direct demonstration of the utility of two-dimensional layer materials in energy conversion devices.

2 Experiment and analysis We prepare monolayer and multilayer h-BN, grown by chemical vapor deposition (CVD) on a copper (Cu) surface [6]. Then metal grown substrate is etched away and the h-BN layer is released onto the etchant solution surface [7]. Afterwards, this released h-BN layer is picked up and placed into a perovskite solution, $CH_3NH_3SnI_3$. This step requires very careful handling due to possible contamination and to prevent possible exudation on the top surface of h-BN. Next, the h-BN layer with solution is dropped onto a glass substrate and spin coated at 1500 rpm, in a glove box, to remove excessive perovskite solution underneath the h-BN layer. This process is very delicate and it is subjected to significant environmental influences. The main effort aims to keep the h-BN layer as flat as possible without any folding or dramatic orientation change. Then, the second perovskite layer, $CH_3NH_3PbI_{3-x}Br_x$, is spin coated (3000 rpm) onto the h-BN layer. Finally, the sample is annealed at 60 °C for 15 min.

Figure 1a shows schematically the stacked architecture of the graded band gap perovskite material. In the first

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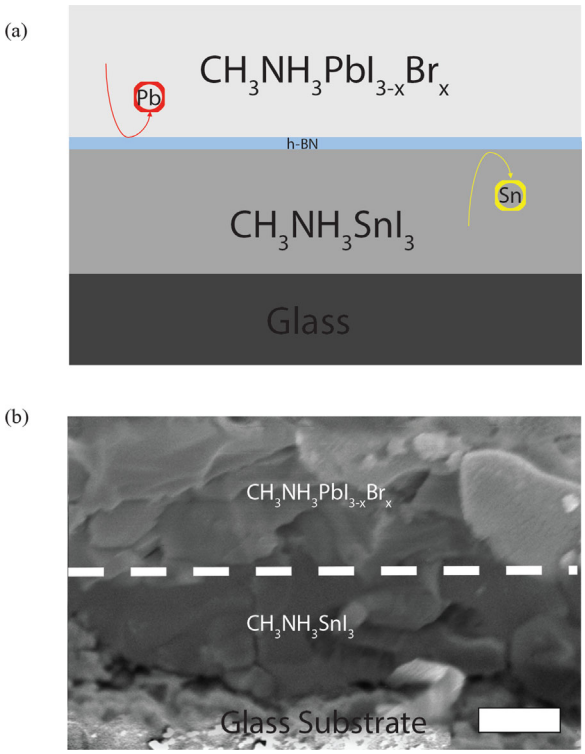

Figure 1 (a) Schematic of a graded band gap perovskite layer. (b) Cross-sectional scanning electron microscopy (SEM) image of a representative double layer perovskite. Approximate position of the monolayer h-BN between perovskite layers is marked with dashed line (not visible in this SEM image). Thickness of $CH_3NH_3SnI_3$ is 200 nm and $CH_3NH_3PbI_{3-x}Br_x$ is 300 nm. The scale bar is 100 nm.

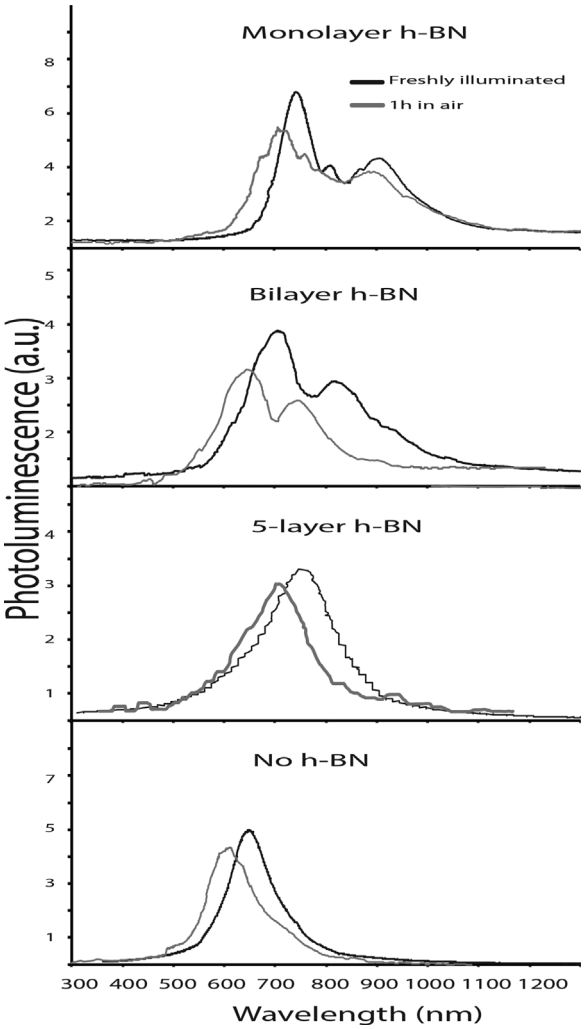

Figure 2 Photoluminescence (PL) spectra of perovskite cells with different h-BN layer thicknesses. The PL data also includes time-dependent behavior of the cells, freshly illuminated cells and cells that waited in air for 1 h. Cells with h-BN show multi peak formation which can be correlated with graded band gap formation. Cells without h-BN layer exhibit one single recombination location and no graded formation is observed. The multi peak formation still exists even after 1 h in ambient air.

perovskite layer, using Sn as a metal cation results in a band gap formation in the range from 1.2 to 1.5 eV [8–13] and using Pb in the second layer, results in a band gap at 1.5–2.2 eV [14–18], respectively. Variation of the halide concentration tunes the bandgap formation. A cross-sectional scanning electron microscope (SEM) image is shown in Fig. 1b with approximate positioning of the perovskite layers and h-BN.

The photoluminescence (PL) spectra of this double layer perovskite structure are shown in Fig. 2. Peak locations in PL the spectrum occur as a result of carrier recombination and multi peak forms due to recombination at different locations. Perovskite layers with h-BN layer display multi peak characteristics, which are associated with graded band gap formation. Multiple peaks are more prominent when monolayer h-BN is used as a separator and the spectrum is quenched with increasing h-BN layer thickness. The double layer perovskite fabricated without h-BN displays no graded bandgap formation. This emphasizes the importance of h-BN to form a graded band gap. h-BN prevents the mixing of two organic–inorganic halide perovskites and serves as a cationic diffusion barrier. For the sample without h-BN, the $CH_3NH_3SnI_3$ and $CH_3NH_3PbI_{3-x}Br_x$ can be intermixed which lead to Sn–Pb distribution along the sample to form $CH_3NH_3Sn_xPbI_{1-x}Br_3$ [19]. This intermixing is responsible for the shift in the peak between cells with five-layer h-BN and without h-BN. The multi-peaks still exist even after 1 h of ambient air exposure in cells with monolayer and bi-layer h-BN. The blue shift in the emissions after 1 h of air exposure is simply due to compositional change by moisture exposure [16].

Figure 3 shows a cross-sectional line mapping of energy dispersive X-ray spectroscopy (EDAX) of double layers with and without h-BN. The EDAX line scan exhibits Sn and Pb steep concentration gradients at the h-BN interface (Fig. 3a) while iodide (I) and bromide (Br) concentrations gradually decrease and increase, respectively. I and Br are

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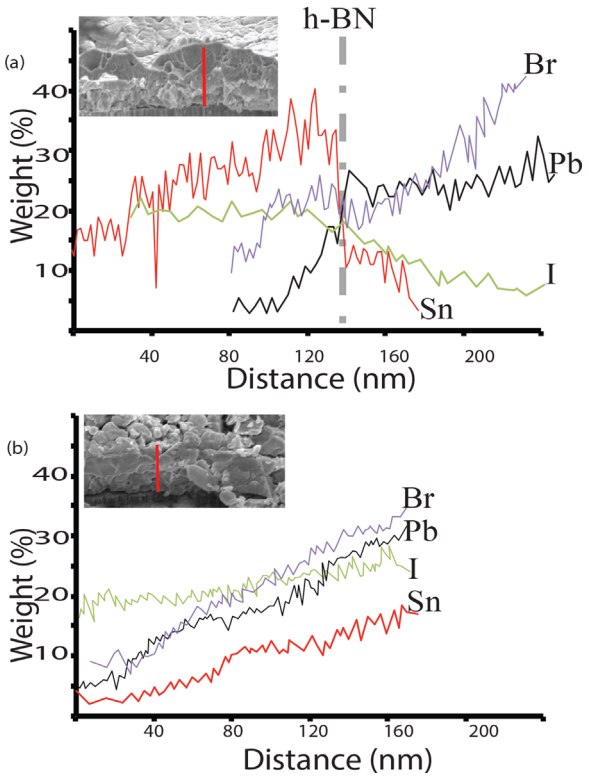

Figure 3 Cross-sectional SEM-EDAX analysis of double layer perovskite cells (a) with h-BN, (b) without h-BN. The line mapping of the cell with h-BN modification (dash-dotted line indicates the position of h-BN) clearly indicates that h-BN acts as a cationic diffusion barrier, especially for Sn and Pb cations. Insets show the SEM image of the line scans.

more probable to diffuse thorough the h-BN layer than Pb and Sn. This line mapping demonstrates the essential role of h-BN as a cationic diffusion barrier to prevent undesired cation mixing, but also controls variation of iodide and bromide concentrations. The layers without h-BN display an upward trend for cation and halide ion distributions. Moreover, there is no steep gradient feature at any Sn and Pb fraction. These indicate Sn, Pb, I, and Br are mixing along the sample (Fig. 3b).

3 Conclusions We have demonstrated a novel technique to produce graded bandgap organohalide perovskite heterostructures. A band gap can be attained in the range 1.2–2.2 eV. h-BN makes an excellent cationic diffusion barrier and plays an important role in realizing graded band gap formation. This technique is generic, and enables a new pathway to material synthesis, growth, and application.

Acknowledgements This research was supported in part by the Director, Office of Science, Office of Basic Energy Sciences, Materials Sciences and Engineering Division of the U.S. Department of Energy under contract no. DE-AC02-05CH11231, which provided for PL measurements under an LDRD award, and, within the sp^2-bonded materials program (KC2207), for the design of the experiment and material characterization; the National Science Foundation under grant 1542741, which provided for perovskite preparation; and by the Office of Naval Research (MURI) under grant N0014-16-1-2229, which provided for h-BN growth. SMG and ST acknowledge support from the NSF Graduate Fellowship Program.

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