ACS OMEGA

http://pubs.acs.org/journal/acsodf

Article

Hexagonal Boron Nitride Seed Layer-Assisted van der Waals Growth of $BaSnO_3$ Perovskite Films

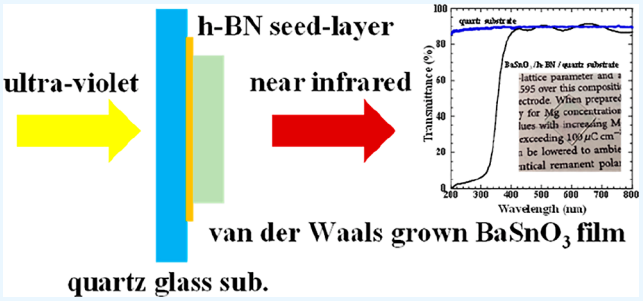
Hiroshi Takashima,* Yoshiyuki Inaguma, Masayoshi Nagao, and Katsuhisa Murakami*

Cite This: *ACS Omega* 2023, 8, 28778−28782

Read Online

ACCESS | Metrics & More | Article Recommendations

ABSTRACT: We have succeeded in obtaining $BaSnO_3$ perovskite thin films with remarkable near-infrared luminescence by van der Waals growth. The films were grown on quartz glass substrates by pulsed laser deposition using hexagonal boron nitride as the seed layer, and their crystallinity was confirmed by X-ray diffraction and cross-sectional transmission electron microscopy. The near-infrared emission of the grown film exhibited a broad emission peak centered at 920 nm. The transparency of the $BaSnO_3$ film (thickness = 1000 nm)/ hexagonal boron nitride /double-sided optically polished quartz glass substrate was approximately 90% at approximately 500 nm with or without the $BaSnO_3$ film. Films showing remarkable near-infrared emission and high transparency obtained by van der Waals-type growth could be used in practical wavelength conversion devices that improve the efficiency of Si single-crystal solar cells. The hexagonal boron nitride seed layer supporting the van der Waals growth is an effective method for high-quality crystal growth of films. It can be used for perovskite-type oxides with many functionalities.



1. INTRODUCTION

Thin-film oxide phosphors can be applied to field emission displays, electroluminescence devices, and wavelength conversion devices in solar cells owing to their excellent chemical and long-term stability, three primary colors of visible light [ultraviolet (UV), blue, green, and red], and near-infrared emission properties.[1,2] Several crystalline perovskite-type oxide phosphors with strong luminescence have been developed in recent years.[3−8] The development of an inexpensive technology for the fabrication of transparent films on glass substrates with excellent practical industrial application of these materials is required. However, these films have lower luminescence intensity owing to their flat interface and lower crystallinity than their bulk powder. Since luminescence and transparency are strongly influenced by the crystallinity, surface structure, and optical band gap of the matrix material, it is important to obtain high-quality crystallinity to obtain high luminescence. The ideal way to control film crystallinity is through epitaxial growth on a single crystal substrate,[9,10] but single crystals are often limited in size and expensive making them unsuitable for industrial applications. In previous studies, crystal growth has been controlled using extremely flat and dense monolayer films prepared using the Langmuir−Blodgett method as the seed layers.[11−14] Moreover, highly bright transparent perovskite-type oxide phosphor films have been experimentally grown on inexpensive quartz glass plates using Langmuir−Blodgett method.[15] This method using a seed layer eliminates the problem of poor crystallinity when directly deposited on glass substrates and enables the application of oxide thin film phosphors using glass substrates, but in an industrial manufacturing process, the entire deposition process should ideally be a vapor phase method. Therefore, in this study, we focused on hexagonal boron nitride (h-BN), which has recently been developed as a high-quality insulating layer by the vapor phase method, as a seed layer, and attempted high-quality crystal growth of heterogeneous layered materials on top of it via van der Waals forces. The crystal structure of h-BN is similar to that of graphite, in which the in-plane boron and nitrogen atoms are linked by strong covalent bonds and the adjacent layers are held together by van der Waals forces.[16,17] The h-BN seed layer had a thickness of approximately 10 nm and a film was grown via van der Waals over it through crystal control. Van der Waals growth is crystal-growth between different layered materials that proceeds via weak van der Waals forces.[18−20]

We selected $BaSnO_3$, which is used as a wavelength conversion material for single-crystal Si solar cells, as the perovskite-type oxide phosphor. In 2004, Mizoguchi et al.[21]

Received: May 25, 2023
Accepted: July 18, 2023
Published: July 25, 2023

reported that a powder sample of $BaSnO_3$ has a cubic perovskite structure and emits strongly in the near-infrared (NIR) region at room temperature with a band gap excitation of 380 nm (3.26 eV). Wavelength conversion from UV to NIR light in sunlight is expected to improve the power generation efficiency since the power generation efficiency of crystalline silicon (c-Si) solar cells is higher in the NIR region. We fabricated epitaxial $BaSnO_3$ films on double-side polished $SrTiO_3$ (001) substrates with a transmittance of 70% (at 500 nm) to explore the possibility of wavelength conversion by the film and reported their crystallinity, emission characteristics, and high efficiency.[22] In this study, h-BN was used as a seed layer on a quartz glass substrate to ensure transparency; a perovskite $BaSnO_3$ film was fabricated on it through vapor phase growth to control its crystallinity and investigate its properties to explore the possibility of practical applications.

2. EXPERIMENTS

Multilayered h-BN was directly synthesized on the substrate using an inductively coupled plasma−chemical vapor deposition system. Details of the deposition and evaluation were described in previous report.[16] In this study, the typical conditions during deposition were as follows: temperature = 500 °C, pressure = 10 Pa, RF input power = 180 W, N_2 flow rate = 15 sccm, and H_2 flow rate = 5 sccm.

A $BaSnO_3$ film was prepared on an h-BN layer by the pulsed laser deposition using a $BaSnO_3$ polycrystalline target. The $BaSnO_3$ polycrystalline target were prepared using the usual solid-phase reaction. The resulting $BaSnO_3$ pellet was confirmed to have a single-phase by powder X-ray diffraction (XRD) measurements. Details of the preparation method were described in previous report.[22] In this study, the thickness of all films were approximately 1000 nm.

The crystallinity of films was studied using XRD. The emission and excitation spectra were measured at room temperature using a spectrofluorometer (Horiba Jobin Yvon, Fluorolog SP NIR). Transmittance in visible and NIR regions was measured using a UV/visible/NIR spectrophotometer (Jasco, V-570). The morphology of the films was observed by atomic force microscopy (AFM; SHIMADSU SPM-9700) with multipoint measurements. The cross-sectional transmission electron microscopy (TEM) images of the $BaSnO_3$/h-BN/quartz glass stack were obtained using FEI Tecnai Osiris with an acceleration voltage of 200 kV.

3. RESULTS

3.1. Crystallinity Evaluation. Figure 1 shows the XRD results of $BaSnO_3$ with several diffraction peaks; no other impurity peaks are observed. This confirms that the film consists of a single phase of polycrystalline $BaSnO_3$. The diffraction peaks of h-BN are not confirmed owing to the thickness of the thin film. In a previous report on $Pr_{0.002}(Ca_{0.6}Sr_{0.4})_{0.997}TiO_3$, direct deposition at 800 °C by PLD on a quartz glass substrate was reported to exhibit amorphous-like crystallinity and no luminescent properties.[15] $BaSnO_3$ was also directly deposited on quartz glass substrate with similar results. This result confirms that the h-BN seed layer contributes significantly to the crystal growth to its top.

Cross-sectional high-resolution TEM (HRTEM) was used to determine the lattice arrangement at each interface and within the film. Figure 2a shows a cross-sectional HRTEM image of the h-BN seed layer and the $BaSnO_3$ film grown on a quartz glass substrate. The polycrystalline $BaSnO_3$ film is further confirmed by the HRTEM results; a multilayered h-BN structure with a thickness of approximately 10 nm was observed between the $BaSnO_3$ film and quartz glass substrate. The interface between the h-BN and $BaSnO_3$ films is clear with no signs of interfacial reactions. This confirms that $BaSnO_3$ has a van der Waals growth on the h-BN seed layer. Figure 2b shows a cross-sectional TEM image of the thick $BaSnO_3$ film at the center. It can be observed that the crystal axes are partially oriented in the same direction. No depletion or defects are observed indicating that a high-quality $BaSnO_3$ film has grown on the h-BN seed layer.

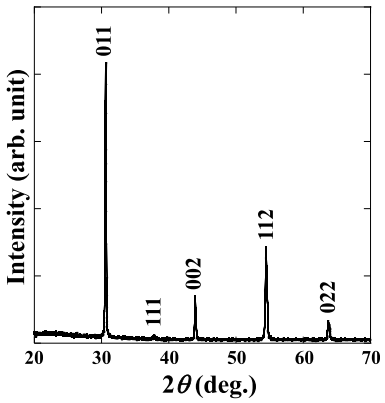


Figure 1. XRD of the h-BN seed layer of the $BaSnO_3$ film grown on the quartz glass substrate. Multiple diffraction peaks of $BaSnO_3$ are observed with no impurity peaks confirming that the thin film is composed only of highly polycrystalline $BaSnO_3$. The diffraction peaks of the h-BN layer could not be confirmed due to the thin film thickness.

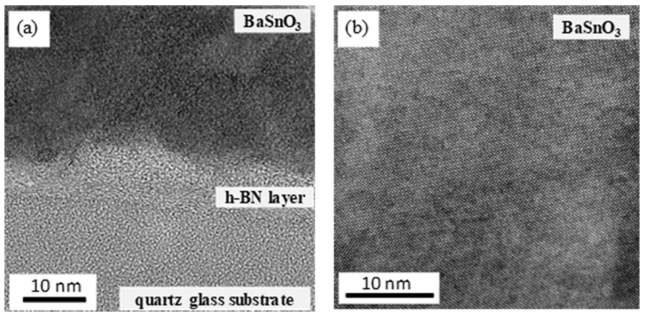


Figure 2. (a) The cross-sectional HRTEM image of the h-BN seed layer of the $BaSnO_3$ film grown on the quartz glass substrate. A polycrystalline $BaSnO_3$ film is formed, and an h-BN layer of around 10 nm thickness is observed between the $BaSnO_3$ film and quartz glass substrate. The h-BN seed layer has a clear layered structure. (b) Cross-sectional TEM image of the $BaSnO_3$ film just at the center of the film thickness. Crystal axes are partially oriented in the same direction and no depletion or defects are observed.

3.2. PL Characteristics. The luminescence properties of the van der Waals grown $BaSnO_3$ films were investigated. Figure 3a shows the emission spectra (PL) of films grown at 700 °C under UV excitation (λ_{ex} = 335 nm). Immediately after the growth, the film shows a broad emission peak centered at 920 nm with a full width at half maximum of 120 nm and tails extending to approximately 800 and 1200 nm. Previous studies[21] using powder samples have concluded that the emission in the NIR region originates from the intrinsic defect centers in $BaSnO_3$. Our results also suggest that intrinsic defect

https://doi.org/10.1021/acsomega.3c03666
ACS Omega 2023, 8, 28778−28782

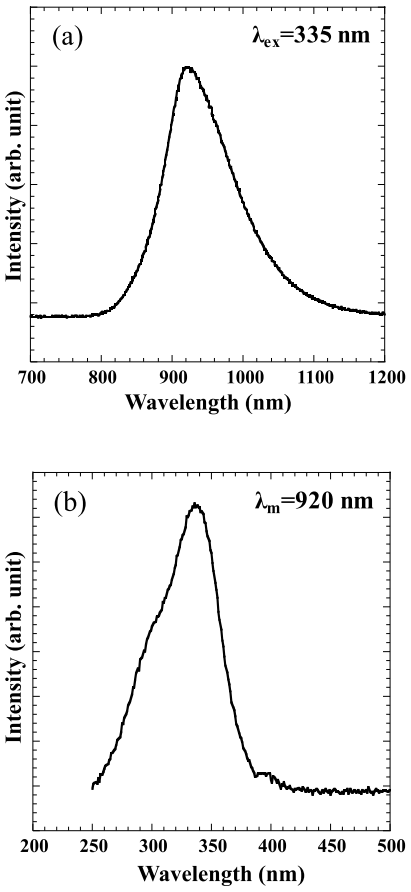


Figure 3. (a) Emission spectra (PL) under UV excitation (λ_{ex} = 335 nm) of films grown on a substrate heated at 700 °C. The film immediately after its growth shows a broad emission peak centered at 920 nm with a full width at half maximum of 120 nm and tails extending to about 800 and 1200 nm. (b) The excitation spectrum (PLE) in which the excitation peak is centered at 335 nm and tails extending to 250 nm and about 420 nm.

centers in the $BaSnO_3$ film are generated during film preparation and in the powder sample. The excitation spectrum (PLE) during the growth is shown in Figure 3b with an excitation peak centered at 335 nm and tails extending to 250 and 420 nm. The luminescence properties are similar to those of epitaxial growth indicating excellent crystallinity.[22] These results indicate that near-infrared light can be excited by ultraviolet light in sunlight, suggesting that it can be used as a wavelength converter to improve the efficiency of photovoltaic power generation.

3.3. Evaluation of Transparency. Transmittance was measured in UV, visible, and NIR regions using UV, visible, and NIR spectrophotometers, respectively. The transmittance spectra of the quartz glass substrate and typical $BaSnO_3$ (001) film are shown in Figure 4. The quartz glass substrate exhibits a high transmittance of 90% at approximately 500 nm. In the UV region, the $BaSnO_3$ film cannot transmit UV light owing to the band gap of 3.2 eV.[23,24] Despite the thickness of the $BaSnO_3$ film of 1000 nm, transmittance in the visible light region is approximately equal to that of the quartz glass substrate, indicating the formation of a high-quality film with excellent transmission characteristics. The inset shows a transmission photograph of $BaSnO_3$ (t = 1000 nm)/h-BN(t = 10 nm)/ quartz glass substrate (t = 0.5 mm), in which the characters are

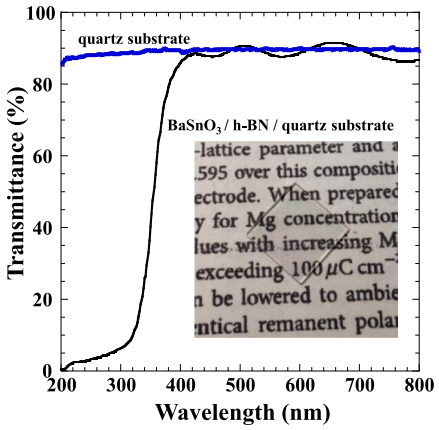


Figure 4. The transmittance spectra of the h-BN seed layer of the $BaSnO_3$ film grown on the quartz glass substrate. The quartz glass substrate shows a high transmittance of 90% around 500 nm. The $BaSnO_3$ film failed to transmit UV light due to its band gap of 3.2 eV. Despite the thickness of the $BaSnO_3$ film of 1000 nm, the transmittance in the visible light region is almost equal to that of the quartz glass substrate, indicating a high-quality film with excellent transmission characteristics. The inset shows a transmission photograph of $BaSnO_3$ (t = 1000 nm)/h-BN/ quartz glass substrate (t = 0.5 mm).

visible due to excellent transparency, thereby confirming the fabrication of high-quality films and interfaces.

4. DISCUSSIONS

The morphology of the film was observed by multipoint measurements using an atomic force microscope (AFM) to investigate the decrease in transmittance owing to the diffuse reflection of light on the film surface. Figure 5a shows a typical

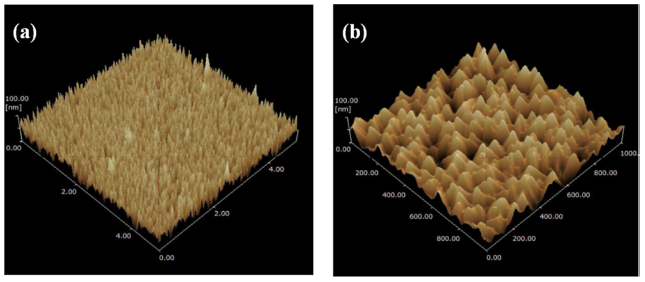


Figure 5. (a) The AFM image of a 1000 nm thick $BaSnO_3$ film grown at 700 °C under 10 Pa oxygen gas on the h-BN seed layer. The measurement range is 5 μm × 5 μm, and the height is 100 nm. (b) AFM image with a measurement range of 1 μm × 1 μm and a height of 100 nm. Surface morphology dominated by a triangular pyramid structure with about 50 nm on each side. The calculated average roughness R_a is 13.3 nm.

AFM image of a 1000 nm-thick $BaSnO_3$ film grown on the h-BN layer at 700 °C under 10 Pa oxygen gas. The measurement range is 5 μm × 5 μm, and the height is 100 nm. Figure 5b shows an AFM image with a measurement range of 1 μm × 1 μm and a height of 100 nm dominated by a triangular pyramid structure of approximately 50 nm on each side. The calculated average roughness (R_a) is 13.3 nm. This high value is attributed to the film thickness of 1000 nm; a structure of approximately 50 nm suppresses the diffuse reflection of light on the film surface, thus ensuring transparency.

https://doi.org/10.1021/acsomega.3c03666
ACS Omega 2023, 8, 28778−28782

$BaSnO_3$ films are grown on quartz glass substrates by pulsed laser deposition using h-BN as the seed layer resulting in good crystallinity and optical properties. The results are similar to the crystallinity and optical properties of $BaSnO_3$ epitaxially grown on $SrTiO_3$ (001).[22] $BaSnO_3$ films are grown on quartz glass substrates by pulsed laser deposition under similar conditions without an h-BN seed layer. The crystallinity of $BaSnO_3$ films was verified by XRD which revealed nearly amorphous structures without any luminescence. In addition, the films were cloudy and good transmittance could not be obtained. Perovskite oxide thin film Pr-$CaSrTiO_3$ gave similar experimental results when deposited on quartz glass substrates.[15] Crystals growing on single-crystal substrates and nanosheets are strongly bonded to the underlying material by ionic and covalent bonds and are susceptible to lattice effects. However, h-BN is a two-dimensional layered material, and weak van der Waals forces are dominant at the interface. This may allow lattice growth that deviates significantly from the lattice matching rule. In this work, $BaSnO_3$ films grown by van der Waals growth on quartz glass substrates with h-BN as the seed layer formed polycrystals with excellent transparency and exhibited remarkable NIR emission, comparable to that of films grown on single-crystal substrates.

5. CONCLUSIONS

$BaSnO_3$ films were grown on quartz glass substrates by pulsed laser deposition using h-BN as the seed layer and their crystallinity was confirmed by XRD. The NIR emission of the grown film exhibited a broad emission peak centered at 920 nm. The transparency of the $BaSnO_3$ film (thickness = 1000 nm)/h-BN/double-sided film on optically polished quartz glass substrate was about 90% at about 500 nm with and without the film, suggesting that the transmittance of the film alone is close to 100%. Crystal growth on single-crystal substrates and nanosheets is strongly bonded to the substrate by ionic and covalent bonds and is susceptible to lattice mismatch. On the other hand, h-BN is a two-dimensional layered material, and relatively weak van der Waals bonds dominate at the interface, allowing lattice growth deviating from lattice matching. $BaSnO_3$ films grown via van der Waals growth on quartz glass substrates with h-BN as seed films have been successfully confirmed to grow as polycrystals with excellent transparency and remarkable NIR luminescence comparable to that of the bulk. Films exhibiting strong NIR luminescence and high transparency due to van der Waals growth are useful for application in wavelength conversion devices that can improve the efficiency of Si single-crystal solar cells. Furthermore, the h-BN seed layer supporting the growth of van der Waals growth is an effective method for thin film growth. The widespread practical applications of perovskite oxides is based on their different properties: luminescence properties, dielectric properties, ferroelectric properties, superconductivity, giant magnetoresistance, ferromagnetism, and multiferroelectricity.

AUTHOR INFORMATION

Corresponding Authors

Hiroshi Takashima − *National Institute of Advanced Industrial Science and Technology, Tsukuba, Ibaraki 305-8568, Japan;* orcid.org/0000-0002-3437-468X; Email: h-takashima@aist.go.jp

Katsuhisa Murakami − *National Institute of Advanced Industrial Science and Technology, Tsukuba, Ibaraki 305-8568, Japan;* orcid.org/0000-0001-5999-5581; Email: murakami.k@aist.go.jp

Authors

Yoshiyuki Inaguma − *Department of Chemistry, Faculty of Science, Gakushuin University, Tokyo 171-8588, Japan;* orcid.org/0000-0002-1174-8407

Masayoshi Nagao − *National Institute of Advanced Industrial Science and Technology, Tsukuba, Ibaraki 305-8568, Japan*

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.3c03666

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This study was partly supported by JSPS KAKENHI (Grant No. JP20H00314, and JP 21H01401).

REFERENCES

(1) Yen, W. M.; Shionoya, S.; Yamamoto, H. *Phosphor Handbook*; CRC Press: New York, 2006.

(2) Takashima, H.; Shimada, K.; Miura, N.; Katsumata, T.; Inaguma, Y.; Ueda, K.; Itoh, M. Low-Driving-Voltage Electroluminescence in Perovskite Films. *Adv. Mater.* **2009**, *21*, 3699−3702.

(3) Okamoto, S.; Yamamoto, H. Characteristic enhancement of emission from $SrTiO_3:Pr^{3+}$ by addition of group-III*b* ions. *Appl. Phys. Lett.* **2001**, *78*, 655−657.

(4) Kyomen, T.; Sakamoto, R.; Sakamoto, N.; Kunugi, S.; Itoh, M. Photoluminescence Properties of Pr-Doped (Ca, Sr, Ba)TiO_3. *Chem. Mater.* **2005**, *17*, 3200−3204.

(5) Inaguma, Y.; Nagasawa, D.; Katsumata, T. Photoluminescence of Praseodymium-Doped $Sr_{n+1}TinO_{3n+1}$ (n=1, 2, ∞). *Jpn. J. Appl. Phys.* **2005**, *44*, 761−764.

(6) Yamamoto, H.; Mikami, M.; Shimomura, Y.; Oguri, Y. Host-to-activator energy transfer in a new blue-emitting phosphor $SrHfO_3:Tm^{3+}$. *J. Lumin.* **2000**, *87*−*89*, 1079−1082.

(7) Shimizu, Y.; Takano, Y.; Ueda, K. UV emission from Gd^{3+} ions in Gd^{3+}−Pr^{3+} codoped $YAlO_3$ perovskite. *J. Lumin.* **2013**, *141*, 44−47.

(8) Ueda, K.; Yamashita, T.; Nakayashiki, K.; Goto, K.; Maeda, T.; Furui, K.; Ozaki, K.; Nakachi, Y.; Nakamura, S.; Fujisawa, M.; Miyazaki, T. Green, Orange, and Magenta Luminescence in Strontium Stannates with Perovskite-Related Structures. *Jpn. J. Appl. Phys.* **2006**, *45*, 6981−6983.

(9) Takashima, H.; Ueda, K.; Itoh, M. Red photoluminescence in praseodymium-doped titanate perovskite films epitaxially grown by pulsed laser deposition. *Appl. Phys. Lett.* **2006**, *89*, 261915−261917.

(10) Ueda, K.; Maeda, T.; Nakayashiki, K.; Goto, K.; Nakachi, Y.; Takashima, H.; Nomura, K.; Kajihara, K.; Hosono, H. Photoluminescence from Epitaxial Films of Perovskite-type Alkaline-earth Stannates. *Appl. Phys. Express* **2008**, *1*, 015003−015005.

(11) Kuroda, K.; Sasaki, T. *Science and Applications of Inorganic Nanosheets*; CMC Press: Tokyo, 2005.

(12) Schaak, R. E.; Mallouk, T. E. Self-assembly of Tiled Perovskite Monolayer and Multilayer Thin Films. *Chem. Mater.* **2000**, *12*, 2513−2516.

(13) Muramatsu, M.; Akatsuka, K.; Ebina, Y.; Wang, K.; Sasaki, T.; Ishida, T.; Miyake, K.; Haga, M. Fabrication of Densely Packed Titania Nanosheet Films on Solid Surface by Use of Langmuir−Blodgett Deposition Method without Amphiphilic Additives. *Langmuir* **2005**, *21*, 6590−6595.

(14) Shibata, T.; Fukuda, K.; Ebina, Y.; Kogure, T.; Sasaki, T. One-Nanometer-Thick Seed Layer of Unilamellar Nanosheets Promotes Oriented Growth of Oxide Crystal Films. *Adv. Mater.* **2008**, *20*, 231−235.

https://doi.org/10.1021/acsomega.3c03666
ACS Omega 2023, 8, 28778−28782

(15) Tetsuka, H.; Takashima, H.; Ikegami, K.; Nanjo, H.; Ebina, T.; Mizukami, F. Nanosheet Seed-Layer Assists Oriented Growth of Highly Luminescent Perovskite Films. *Chem. Mater.* **2009**, *21*, 21−26.
(16) Yamamoto, M.; Murata, H.; Miyata, N.; Takashima, H.; Nagao, M.; Mimura, H.; Neo, Y.; Murakami, K. Low-Temperature Direct Synthesis of Multilayered h-BN without Catalysts by Inductively Coupled Plasma-Enhanced Chemical Vapor Deposition. *ACS Omega* **2023**, *8*, 5497−5505.
(17) Murakami, K.; Igari, T.; Mitsuishi, K.; Nagao, M.; Sasaki, M.; Yamada, Y. Highly Monochromatic Electron Emission from Graphene/Hexagonal Boron Nitride/Si Heterostructure. *ACS Appl. Mater. Interfaces* **2020**, *12*, 4061−4067.
(18) Jiang, J.; Bitla, Y.; Huang, C. W.; Do, T. H.; Liu, H. J.; Hsieh, Y. H.; Ma, C. H.; Jang, C. Y.; Lai, Y. H.; Chiu, P. W.; Wu, W. W.; Chen, Y. C.; Zhou, Y. C.; Chu, Y. H. Flexible ferroelectric element based on van der Waals heteroepitaxy. *Sci. Adv.* **2017**, *3*, No. e1700121.
(19) Koma, A. Van der Waals epitaxy for highly lattice-mismatched systems. *J. Cryst. Growth* **1999**, *201−202*, 236−241.
(20) Koma, A.; Saiki, K.; Sato, Y. Heteroepitaxy of a two-dimensional material on a three-dimensional material. *Appl. Surf. Sci.* **1990**, *41−42*, 451−456.
(21) Mizoguchi, H.; Woodward, P. M.; Park, C.-H.; Keszler, D. A. Strong Near-Infrared Luminescence in $BaSnO_3$. *J. Am. Chem. Soc.* **2004**, *35*, 9796−9800.
(22) Takashima, H.; Inaguma, Y. Near-infrared luminescence in perovskite $BaSnO_3$ epitaxial films. *Appl. Phys. Lett.* **2017**, *111*, 0919031−0919033.
(23) Mizoguchi, H.; Eng, H. W.; Woodward, P. M. Probing the Electronic Structures of Ternary Perovskite and Pyrochlore Oxides Containing Sn^{4+} or Sb^{5+}. *Inorg. Chem.* **2004**, *35*, 1667−1680.
(24) Schumann, T.; Raghavan, S.; Ahadi, K.; Kim, H.; Stemmer, S. Structure and optical band gaps of $(Ba,Sr)SnO_3$ films grown by molecular beam epitaxy. *J. Vac. Sci. Technol. A* **2016**, *34*, 0506011−0506014.

https://doi.org/10.1021/acsomega.3c03666
ACS Omega 2023, 8, 28778−28782