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Photon Transport in One-Dimensional Incommensurately Epitaxial $CsPbX_3$ Arrays

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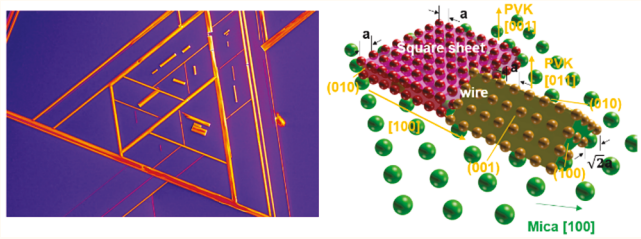
S *Supporting Information*

ABSTRACT: One-dimensional nanoscale epitaxial arrays serve as a great model in studying fundamental physics and for emerging applications. With an increasing focus laid on the Cs-based inorganic halide perovskite out of its outstanding material stability, we have applied vapor phase epitaxy to grow well aligned horizontal $CsPbX_3$ (X: Cl, Br, or I or their mixed) nanowire arrays in large scale on mica substrate. The as-grown nanowire features a triangular prism morphology with typical length ranging from a few tens of micrometers to a few millimeters. Structural analysis reveals that the wire arrays follow the symmetry of mica substrate through incommensurate epitaxy, paving a way for a universally applicable method to grow a broad family of halide perovskite materials. The unique photon transport in the one-dimensional structure has been studied in the all-inorganic Cs-based perovskite wires via temperature dependent and spatially resolved photoluminescence. Epitaxy of well oriented wire arrays in halide perovskite would be a promising direction for enabling the circuit-level applications of halide perovskite in high-performance electro-optics and optoelectronics.



KEYWORDS: *Halide, perovskite, incommensurate, epitaxy, photon, transport*

Hybrid organic−inorganic halide perovskite has proven displaying promising properties[1−7] in the photovoltaic field where effective charge separation and transport are keys to a favorable device performance. Recently, the photon recycling phenomenon of the organic perovksite material has been studied.[8] It turns out that the reabsorption of the self-emitted photons and the subsequent regeneration of new ones gives rise to longer effective charge diffusion lengths. However, alongside the success of the hybrid perovskite material comes the degradation issue[9−14] partially due to the volatile nature of the organic group. The inorganic alkali metal halide perovskite is thereafter introduced as a substitute to enhance the material stability.[15,16] Under such scenario comes the need to investigate the photon transport properties in the inorganic material system to further evaluate the application prospect in similar fields. Experimentally, a one-dimensional (1D) wire structure would be most favorable for such a study where the mathematical description of the transport is simple and at the same time, the photons are confined inside the structure[17] to minimize the loss from scattering effects.

In general, the 1D wire structure itself shows uniquely promising applications in various fields[18] including superlattice heterojunction devices,[19] field effect transistors,[20] light-emitting diodes,[21] lasers[22−27] (recently demonstrated in individual hybrid perovskite[22,23] and also inorganic $CsPbX_3$[27] nanowire synthesized by other approaches), sensors[28] and energy converters.[29,30] However, for circuit level application it requires stringent alignment of wires, often in a horizontal manner.[18] Unfortunately, the precise lateral (or horizontal) alignment of wires has always remained a critical issue. The problem is often tackled by post transfer or treatment where you introduce external stimuli (mechanical force,[31] electric field,[32,33] magnetic field,[34] chemical reactions,[35] electrostatic force[36]) to align wires.[37,38] For more precise lateral orientation control, conventional chemical/ionic epitaxy concept has been often applied.[39,40] In this paper, we introduce a concept of incommensurate van der Waals (VDW) epitaxy for growing and aligning halide perovskite nanowire arrays to enable nanowires for potential circuit level application.

In this manuscript, we successfully achieved epitaxial growth of individual $CsPbX_3$ wire from vapor phase deposition (with X component continuously tuned from Br to I) and large-scale

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Epitaxial Halide Perovskite Lateral Double Heterostructure

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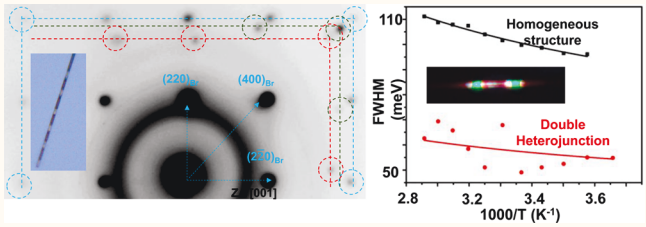
Supporting Information

ABSTRACT: Epitaxial III–V semiconductor heterostructures are key components in modern microelectronics, electro-optics, and optoelectronics. With superior semiconducting properties, halide perovskite materials are rising as promising candidates for coherent heterostructure devices. In this report, spinodal decomposition is proposed and experimentally implemented to produce epitaxial double heterostructures in halide perovskite system. Pristine epitaxial mixed halide perovskites rods and films were synthesized via van der Waals epitaxy by chemical vapor deposition method. At room temperature, photon was applied as a knob to regulate the kinetics of spinodal decomposition and classic coarsening. By this approach, halide perovskite double heterostructures were created carrying epitaxial interfaces and outstanding optical properties. Reduced Fröhlich electron–phonon coupling was discovered in coherent halide double heterostructure, which is hypothetically attributed to the classic phonon confinement effect widely existing in III–V double heterostructures. As a proof-of-concept, our results suggest that halide perovskite-based epitaxial heterostructures may be promising for high-performance and low-cost optoelectronics, electro-optics, and microelectronics. Thus, ultimately, for practical device applications, it may be worthy to pursue these heterostructures via conventional vapor phase epitaxy approaches widely practised in III–V field.



KEYWORDS: *halide perovskites, double heterostructures, spinodal decomposition, nucleation, coarsening*

The beautiful design of semiconductor heterostructures with coherent interfaces that manipulate the semiconductors' energy band landscape by breaking their translational symmetry[1] has realized a powerful control of lasing dynamics,[2] charge transport behaviors,[3] and electron–phonon coupling mechanisms[4] within the device. For example, with heterostructures, challenging requirements critical for electro-optics like efficient population inversion[2] modified electron–phonon coupling[4] and enhanced carrier mobility[5] have been achieved that would be otherwise impossible in a single material system. Practically over the past decades, the III–V and II–VI semiconductor families, with their favorable intrinsic properties, lattice mismatch, and crystal symmetry,[6−8] have always been the most popular candidates for heterostructure fabrication thanks to the advances in vapor phase epitaxy growth techniques such as molecular beam epitaxy (MBE) and metal–organic vapor phase epitaxy (MOCVD).[4,9,10] Accordingly, the laboratory realization and market commercialization of heterostructure transistors,[11] light-emitting diodes (LED),[12] avalanche photodetector,[13] quantum well lasers,[14] double heterostructure lasers,[15] and superlattice-based quantum cascade lasers[16] have been achieved. Recently, the discovery of one class of promising materials has added other possibilities to the heterojunction candidates. The fabrication of two-dimensional transition metal dichalcogenides coherent heterojunction[17,18] has been under intensive investigation in the field that witnesses physical properties like interlayer exciton and long-lived charge carriers.[19]

A similar story is being unfolded in halide perovskites. Starting as a promising solar cell material in photovoltaic field,[20] the lead halide perovskites have been later used in applications like photodetector and sensor,[21,22] LED,[23−27] and optically pumped lasers.[28,29] More insights have also been cast into the deep physics lying behind the superior device performance and unveiled intrinsic material properties like carrier lifetime exceeding 100 μs[30] that outperform the conventional III–V and II–VI family.[4] The success and rapid development in the perovskite field would therefore favor the

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High-Temperature Ionic Epitaxy of Halide Perovskite Thin Film and the Hidden Carrier Dynamics

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Abstract

High-temperature vapor phase epitaxy (VPE) has been proved ubiquitously powerful in enabling high-performance electro-optic devices in III-V semiconductor research and industrial community. A typical example is the successful growth of p-type GaN by VPE for blue light emitting diodes. VPE excels as it well controls the film defects such as point defects, grain boundary and interphase defects, thanks to its high-temperature processing condition and controllable deposition rate. In this report, for the first time, we have demonstrated single crystalline high-temperature VPE halide perovskite thin film – a unique platform on unveiling previously uncovered hidden carrier dynamics in inorganic halide perovskite materials. Towards wafer scale epitaxial and grain boundary-free film is grown with alkaline halides as substrates. We show the metal alkali halides could be used as a universal substrate for the VPE growth of perovskite due to their similar material chemistry and close crystal symmetry and lattice constant. With VPE, hot photoluminescence and nanoseconds photo Dember effect were revealed in inorganic halide perovskite. These two phenomena suggest that inorganic halide perovskite could be as compelling as its organic-inorganic counterpart in terms of optoelectronic properties and help explain the long carrier lifetime in halide perovskite. Our findings suggest a new avenue on developing high quality large scale single crystalline halide perovskite films requiring precise control of defects and morphology.

van der Waals epitaxy of CdTe thin film on graphene

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van der Waals epitaxy (vdWE) facilitates the epitaxial growth of materials having a large lattice mismatch with the substrate. Although vdWE of two-dimensional (2D) materials on 2D materials have been extensively studied, the vdWE for three-dimensional (3D) materials on 2D substrates remains a challenge. It is perceived that a 2D substrate passes little information to dictate the 3D growth. In this article, we demonstrated the vdWE growth of the CdTe(111) thin film on a graphene buffered SiO_2/Si substrate using metalorganic chemical vapor deposition technique, despite a 46% large lattice mismatch between CdTe and graphene and a symmetry change from cubic to hexagonal. Our CdTe films produce a very narrow X-ray rocking curve, and the X-ray pole figure analysis showed 12 CdTe (111) peaks at a chi angle of 70°. This was attributed to two sets of parallel epitaxy of CdTe on graphene with a 30° relative orientation giving rise to a 12-fold symmetry in the pole figure. First-principles calculations reveal that, despite the relatively small energy differences, the graphene buffer layer does pass epitaxial information to CdTe as the parallel epitaxy, obtained in the experiment, is energetically favored. The work paves a way for the growth of high quality CdTe film on a large area as well as on the amorphous substrates. *Published by AIP Publishing.*
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Recently, there has been considerable interest in growing epitaxial films on substrates through van der Waals (vdW) interactions.[1] In contrast to the conventional chemical epitaxy where sharing or transferring of electrons occurs at the film-substrate interface, van der Waals epitaxy (vdWE) is based on a physical Coulomb force through the dipole interaction. Since there is no "dangling bond" at the surface under the vdW forces, it is believed that the requirement of lattice matching to grow a defect free film in the conventional chemical epitaxy may be relaxed, and high quality epitaxial films can be grown even when the lattice mismatch between the film and substrate is very large. This implies that strain is completely relaxed at the interface during a growth, even at the first monolayer. To date, there are many examples of vdWE of a two-dimensional (2D) layered material on another 2D layered material. However, vdWE of a three-dimensional (3D) material on a 2D layered material is much more challenging[2] and has only limited success.[3–5] A fundamental challenge is that, by the very nature of weak vdW interactions, a typical 3D material would not "wet" the vdW surface to form a uniform, planar film during growth. Sometimes defects are needed to be created at the 2D layered material to induce many nucleation sites in order to grow a 3D film.[6] For example, large surface step structures have been used to promote the nucleation of GaN islands on the graphene/SiC surface.[3] Another attempt is to deliberately create defects by UV irradiation on the graphene surface to induce many nucleation sites in order to grow a 3D CdTe film.[6] In doing so, the quality of the film deteriorated and the film did not exhibit an epitaxial structure. In this paper, we report the growth of epitaxial CdTe film on a graphene surface without pre-treatment using metalorganic chemical vapor deposition (MOCVD) technique.

Graphene is perhaps the most well-known 2D layered material. It has been actively researched, and it possesses many remarkable electronic and optoelectronic properties.[7] Graphene on a substrate is commercially available. Typically, it is grown by chemical vapor deposition (CVD) technique on a Cu foil and then transferred to a SiO_2/Si substrate.[8,9] Since the Cu foil is not a single crystal, the nucleation of graphene at different regions would possess different orientations. The net result is that the graphene grown on the Cu foil is polycrystalline. However, it was shown that the orientation of the graphene grains is not completely random.[10,11] In fact, the grains often show two dominant orientations with a 30° rotation with respect to each other, and each orientation exhibits a small angular dispersion. The substrate we used is a commercially available graphene film grown by CVD on the Cu foil and then transferred to a SiO_2 (285 nm)/Si substrate.

CdTe has been one of the most popular II–VI semiconductors for its application in photovoltaics, aerospace, and radiation detection based applications. vdWE of CdTe has been attempted earlier on a few 2D materials such as $NbSe_2$, $MoTe_2$, and WSe_2.[4,12] However, graphene as a buffer layer material holds many advantages, such as high thermal stability, high optical transparency, and high electrical conductivity, by ease of producing high quality graphene and ease of

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Full Length Article

Surface and interface of epitaxial CdTe film on CdS buffered van der Waals mica substrate

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ABSTRACT

Single crystal CdTe films are desirable for optoelectronic device applications. An important strategy of creating films with high crystallinity is through epitaxial growth on a proper single crystal substrate. We report the metalorganic chemical vapor deposition of epitaxial CdTe films on the CdS/mica substrate. The epitaxial CdS film was grown on a mica surface by thermal evaporation. Due to the weak van der Waals forces, epitaxy is achieved despite the very large interface lattice mismatch between CdS and mica (~21–55%). The surface morphology of mica, CdS and CdTe were quantified by atomic force microscopy. The near surface structures, orientations and texture of CdTe and CdS films were characterized by the unique reflection high-energy electron diffraction surface pole figure technique. The interfaces of CdTe and CdS films and mica were characterized by X-ray pole figure technique and transmission electron microscopy. The out-of-plane and in-plane epitaxy of the heteroepitaxial films stack are determined to be CdTe(111)//CdS(0001)//mica(001) and $[\bar{1}2\bar{1}]_{CdTe}//[\bar{1}100]_{CdS}//[010]_{mica}$, respectively. The measured photoluminescence (PL), time resolved PL, photoresponse, and Hall mobility of the CdTe/CdS/mica indicate quality films. The use of van der Waals surface to grow epitaxial CdTe/CdS films offers an alternative strategy towards infrared imaging and solar cell applications.

1. Introduction

CdTe has become one of the most important materials in optoelectronic devices, ranging from infrared imaging to solar cell devices. CdTe has a direct band gap at ~1.5 eV and high absorption coefficients ($>5\times10^5$ cm^{-1}) for wavelengths in the solar spectrum. Quality of the CdTe films, in most cases the crystallinity, plays an important role in the performance of the devices. One of the most important strategies to create high crystallinity films is to grow them epitaxially on single crystal substrates. The techniques used to grow CdTe films are rich, including but not limited to molecular beam epitaxy [1,2], e-beam evaporation [3], hot wall epitaxy [4], close space sublimation [5], high vacuum evaporation [6], chemical bath deposition [7], and metalorganic chemical vapor deposition [8]. Examples of single crystal substrates used are Si [2,4,9,10], Ge [1,3,5,8,11], CdTe [12,13], CdS [12,14], GaAs [8,15–21], Al_2O_3 [22], and $SrTiO_3$ [23]. Epitaxial CdTe film has also been shown to grow on glass substrate using nanostructured buffer layer of Ge(111)/CaF_2(111) [24]. Biaxial CdTe films have also been shown to grow on large grain biaxial Ni(100) foils [25,26] and biaxial CaF_2(111) on glass substrate [27]. All these substrates used in the epitaxy growth are either bulk single crystals or epitaxial films that themselves are grown epitaxially on different bulk single crystals, biaxial foils or biaxial films on nanostructures.

In this work, we have adopted a different strategy to develop a relevant substrate for the epitaxial growth of CdTe films, namely the epitaxial CdS films grown on mica substrates through van der Waals epitaxy (vdWE). It has been suggested that substrate with weak van der Waals interaction at interfaces could be a promising strategy for the growth of epitaxial films [28] or nanostructures [29,30], even when the film itself is non-layered in nature. Due to the weak van der Waals interactions, there exists a high tolerance for lattice mismatch between the films and the substrates and strain-free or nearly strain-free films can be achieved even

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