Incommensurate van der Waals Epitaxy of Nanowire Arrays: A Case Study with ZnO on Muscovite Mica Substrates

Muhammad Iqbal Bakti Utama,† Francisco J. Belarre,‡ Cesar Magen,§ Bo Peng,† Jordi Arbiol,*‡∥ and Qihua Xiong*†⊥
†Division of Physics and Applied Physics, School of Physical and Mathematical Sciences, Nanyang Technological University, Singapore 637371
‡Institut de Ciencia de Materials de Barcelona, ICMAB-CSIC, Campus de la UAB, 08193 Bellaterra, Catalonia, Spain
§Laboratorio de Microscopias Avanzadas (LMA), Instituto de Nanociencia de Aragon (INA) - ARAID and Departamento de Fisica de la Materia Condensada, Universidad de Zaragoza, 50018 Zaragoza, Spain
∥Institució Catalana de Recerca i Estudis Avançats (ICREA), 08010 Barcelona, Catalonia, Spain
⊥Division of Microelectronics, School of Electrical and Electronic Engineering, Nanyang Technological University, Singapore 639798

ABSTRACT: The requirement of lattice matching between a material and its substrate for the growth of defect-free heteroepitaxial crystals can be circumvented with van der Waals epitaxy (vdWE). However, the utilization and characteristics of vdWE in nonlamellar/nonplanar nanoarchitectures are still not very well-documented. Here we establish the characteristics of vdWE in nanoarchitectures using a case study of ZnO nanowire (NW) array on muscovite mica substrate without any buffer/seed layer. With extensive characterizations involving electron microscopy, diffraclometry, and the related analyses, we conclude that the NWs grown via vdWE exhibit an incommensurate epitaxy. The incommensurate vdWE allows a nearly complete lattice relaxation at the NW-substrate heterointerface without any defects, thus explaining the unnecessity of lattice matching for well-crystallized epitaxial NWs on muscovite mica. We then determine the polarity of the NW via a direct visualization of Zn−O dumbbells using the annular bright field scanning transmission electron microscopy (ABF-STEM) in order to identify which atoms are at the base of the NWs and responsible for the van der Waals interactions. The information from the ABF-STEM is then used to construct the proper atomic arrangement at the heterointerface with a 3D atomic modeling to corroborate the characteristics of the incommensurate vdWE. Our findings suggest that the vdWE might be extended for a wider varieties of compounds and epitaxial nanoarchitectures to serve as a universal epitaxy strategy.

KEYWORDS: van der Waals epitaxy, heteroepitaxy, nanowire array, nanorods, annular bright field microscopy

In covalent heteroepitaxy, similarity in crystalline symmetry, lattice parameters, and thermal expansion coefficients between the substrate and the epitaxial crystalline overlayer is required to suppress the elastic strain and the nucleation of defects on the crystal.1 Fortunately, the necessity of lattice matching for the well-crystallized overlayer can be alleviated if the adatom-substrate interaction is sufficiently weaker than the lateral adatom-adatom interaction.2 Overlayer with relaxed lattice is thus produced with an incommensurate in-plane lattice at the heterointerface, where a relative in-plane orientation relation with the substrate is still adhered consistently for energy minimization. As an incommensurate epitaxy, van der Waals epitaxy (vdWE) utilizes substrates whose surface is chemically inert due to the absence of dangling bonds (e.g., layered materials) or due to an intentional passivation.3 Hence, the overlayer-substrate interface is mainly mediated by a weak van der Waals force instead of covalent chemical bonds. vdWE thus enables the growth of defect-free lattice-mismatched epitaxial crystal with the bulk lattice constant even from the first monolayer. However, despite the potential for a universal usage, vdWE had mainly been invoked in film growth and lamellar/planar structures4−7 with very limited attribution in other architectures.

We anticipate that vdWE is also applicable in the growth of nonlamellar nanoarchitectures such as vertically aligned nanowire (NW) arrays. Although covalent heteroepitaxial growth in NW array geometry was suggested to relieve strain energy via lateral relaxation owing to the finite diameter of NWs,8 the theoretical upper bound of height and diameter for defect-free...
interface is very limited and is still strongly dependent on lattice mismatch.\(^{5\text{--}14}\) Moreover, excessive strain and defects due to the lattice mismatch may degrade the electronic and photonic properties of the material and compromise the performance of NW array-based devices,\(^{11}\) restraining potential applications utilizing the structures only to homoepitaxy and heteroepitaxy on certain bulk substrates, both of which allow epitaxial NW growth only from limited number of compounds.

In this work, we focus on zinc oxide (ZnO) NW array for the investigation of the epitaxy characteristics of vdWE in NW array, which is essential to validate the reliability of the epitaxy strategy in nanostructural growth. ZnO NW array has been well-characterized and has generated broad interest as one of the most technologically attractive material,\(^{12\text{--}14}\) motivating our choice of ZnO as the model compound. Demonstration with ZnO also expands the class of materials that is preparable as NW array via vdWE, which we previously also believe to be attributable in the growth of other II–VI NW array (CdS, CdSe, CdTe, and ZnTe) with high crystalline and optical quality on muscovite mica.\(^{15\text{--}18}\) Here we also utilized the layer-structured muscovite mica [see Figure S1 in the Supporting Information (SI)] as the substrate, regardless of its lattice mismatch to ZnO, to intentionally manifest the vdWE in the growth of NWs. With its layered structure, where adjacent layers is connected by van der Waals attraction instead of chemical bonds, the freshly cleaved surface of muscovite mica is expected to be free of dangling bonds and is therefore suitable in the demonstration of vdWE.\(^{5\text{--}8,15\text{--}19,20}\) Unlike previous studies of vdWE films, which commonly employs molecular beam epitaxy, our synthesis follows the facile and higher throughput vapor transport technique.\(^{21,22}\) No foreign catalyst introduction and surface treatment of the substrate are necessary for the NW array growth (more details on the synthesis method are available in the SI).

Under an optimal growth environment, the NW array can be exclusively grown at high density and good uniformity over a relatively wide area (\(\sim 1\) cm\(^2\)), as revealed from scanning electron microscopy (SEM) observation (Figure 1a). The cross-sectional view of the sample (Figure 1a inset) further highlights the strong vertical alignment between the NWs. The NWs have uniform diameter throughout their height up to their conical tip. Metal-rich particle, commonly found in a conventional vapor–liquid–solid growth,\(^{23}\) was not observed from both the tip and the base of the NWs (also see Figure S2), as expected from our catalyst-free synthesis approach. The NWs are typically seen to have a diameter in the range of 100–200 nm and a length of around 2–3 \(\mu\)m. As an important observation, the ZnO NWs are singly standing (i.e., disconnected from each other) and the NW-substrate interface is sharp in absence of any buffer layer. The significance of absent buffer layer shall be discussed later in the context of the epitaxy analysis (Figure 2).

The top view SEM image (Figure 1b, inset) shows that the ZnO NWs possess a hexagonal cross-section with an in-plane alignment of the faceting between the NWs. Such in-plane alignment implies that there is a consistency of the crystalline relationship between the atoms at the surface of the substrate and that at the base of all of the NWs, which by themselves also exhibit a consistency in the crystalline faceting (see Figure S3: six planes from the family of \{110\} construct the side facets of the hexagonal cross-section). Therefore, the in-plane alignment strongly suggests that the NWs are grown epitaxially from the substrate. Similar in-plane alignment between the neighboring epitaxial ZnO NWs had also been shown in previous reports.\(^{12,24,25}\) Meanwhile, Figure 1b shows the powder X-ray diffraction pattern of the sample in \(\theta\text{--}\theta\) geometry, where only planes parallel to the surface of the sample contribute to the pattern. The corresponding peaks can be ascribed to the (00 L) basal planes of muscovite mica of 2M\(_1\) polytype \([\text{K}\alpha\text{Al}(\text{SiAl})_2\text{O}_10(\text{OH})_2,\text{monoclinic, space group: C2/c}]\) and to the (0002) and (0004) peaks from wurtzite/zincite ZnO (space group: \(\text{P6}_3\text{mc}\)), whose positions agree well with that of bulk values. Insignificance of other peaks from ZnO confirms that the NWs are well-oriented with a growth direction along the \(c\)-axis.

We proceed to examine the properties and characteristics of vdWE of the ZnO NWs with cross-sectional high resolution transmission electron microscopy (HRTEM) observation. The cross-sectional sample was prepared with focused ion beam (FIB), preceded by a deposition of Au and Pt thin film layer to protect the sample during the ion milling process (also see Materials and Methods in the SI). We chose to observe the region of cross-section which was free of Pt deposits in order to enable correct visualization of the atomic structure of the heterointerface (see the low magnification cross-sectional image in Figure S4).

Figure 1. Morphological characterizations of the vertically aligned ZnO NW array as-grown on muscovite mica substrate. (a) SEM image with 45\(^\circ\) tilted view recorded in low magnification to display the wide-area synthesis. Inset: Cross-sectional (i.e., 90\(^\circ\) tilt) SEM image, showing that the vertical NWs are isolated from each other without any buffer layer at the interface of nanowire-substrate. (b) XRD pattern of the sample in \(\theta\text{--}\theta\) geometry, indexed in blue for ZnO and in red for muscovite mica. Inset: Top view SEM image, revealing the in-plane alignment exhibited between the hexagonal cross-sectioned NWs as clarified by the orange arrows.
The epitaxial relation of the NW-substrate was determined as \((0001)[11\bar{2}0]_{\text{ZnO}} || (001)[01\bar{1}]_{\text{mica}}\) and \((0001)[1\bar{1}00]_{\text{ZnO}} || (001)[10\bar{1}]_{\text{mica}}\) from the color-combined power spectra of the interface (middle-inset of Figure 2a,c). However, the planes of ZnO at the interface which constitute the in-plane vector alignment were mismatched to that of mica as evidenced by the noncoincidence of the Bragg diffraction spots of the two solids; namely, \((1\bar{1}00)_{\text{ZnO}} \rightarrow (200)_{\text{mica}}\) in the middle-inset of Figure 2a as indicated by a white square (also see Figure S5), and \((1\bar{1}\bar{2}0)_{\text{ZnO}} \rightarrow (020)_{\text{mica}}\) in the middle-inset of Figure 2c. In fact, comparing the upper- and lower-inset with the middle-inset of Figure 2a,c, the power spectra at the interface are very close to a simple superimposition of the individual patterns of ZnO and mica. Moreover, the ZnO Bragg diffraction spots appear as isolated spots instead of streak, indicating that the relaxation of ZnO lattice has predominantly occurred at the interface.

The incommensurateness of the ZnO lattices to that of mica at the interface is observable from the Fourier-filtering of the vectorially aligned planes in the HRTEM image (Figure 2b,d). In Figure 2b, the locations where the \((1\bar{1}00)_{\text{ZnO}}\) and the \((200)_{\text{Mica}}\) have a close encounter, but not necessarily a matching, are circled in orange, whereas blue circles mark the locations where the two planes are distantly separated and appear as a mismatch dislocation. The mismatch dislocations are periodic and occur every 12 \((1\bar{1}00)_{\text{ZnO}}\) and 13 \((200)_{\text{Mica}}\) planes. Higher accuracy measurement of the average atomic plane spacing at the interface showed that \(d_{(200)\text{Mica}} = 0.2584\) nm while \(d_{(1\bar{1}00)\text{ZnO}} = 0.2800\) nm. The difference of lattice spacing at the interface even after the epitaxy is formed indicates that our NW-substrate system is of the incommensurate epitaxy (or also commonly called incoherent epitaxy) type instead of the simple coherent heteroepitaxy.

Coherent epitaxy requires that the overlayer be strained to match the lattice spacing of the overlayer to that of the substrate and in order to match the atoms of both solids via a one-to-one mapping, which is not observed in our sample. Defining lattice mismatch by \(f = 100\% \times (1 - d_{\text{overlayer}} / d_{\text{substrate}})\), the present lattice mismatch in \((1\bar{1}00)_{\text{ZnO}} || (200)_{\text{Mica}}\) direction is thus \(-8.36\%\). An even more dramatic lattice mismatch occurred when the other zone axis is considered (Figure 2d): The immensely different lattice spacing of \(d_{(020)\text{Mica}} = 0.4498\) nm and \(d_{(1\bar{1}00)\text{ZnO}} = 0.16175\) nm results in a lattice mismatch of 64.0\% along \([1\bar{1}20]_{\text{ZnO}} \parallel [020]_{\text{mica}}\).

Note that we are concerned with the definition of lattice matching as the matching between individual planes instead of the matching between package of planes (i.e., domain matching), which we believe is not applicable in our system. We assert two interrelated reasons for the exclusion of coherent domain epitaxy, \(^{26}\) which is also a form of conventional heteroepitaxy, in the ZnO-mica sample discussed herein: (i) the presence of mismatch even between the comparably sized domains, and (ii) the absence of buffer layer at the interface. On the first reason, we noticed an experimentally measurable size difference of the domains that would otherwise be perfectly matched at the interface. We measured that the package of planes \(12 \times (1\bar{1}00)_{\text{ZnO}} - 13 \times (200)_{\text{Mica}}\) is actually still mismatched by 0.0008 nm, while the 11 \((1\bar{1}00)_{\text{ZnO}} - 4 \times (020)_{\text{Mica}}\) is still mismatched by 0.01995 nm. Contrary to what would be expected of a coherent domain epitaxy, the ZnO lattices did not accommodate those relatively small mismatches to achieve a perfectly matched epitaxy.

\(2152\)

dx.doi.org/10.1021/nl300554t | Nano Lett. 2012, 12, 2146–2152
As the second reason, it is unusual for such a highly lattice-mismatched system to exhibit an incommensurate epitaxy without any buffer layer or threading dislocations at the interface (Figures 1a and 2a,c). In both thin films and nanostructures that may have small domain mismatch but huge lattice mismatch across individual planes (>10%, e.g., ZnO on a-sapphire), typical domain matching epitaxial systems generally have buffer layer and/or defect-rich interface.\(^{10,26}\) Formation of buffer layer, also commonly called pseudomorphic layer or wetting layer, is a mechanism of strain relaxation in lattice-mismatched heteroepitaxial structures.\(^{27}\) Buffer layer is usually formed spontaneously as a consequence of appreciable NW-substrate lattice mismatch and is often observed in heteroepitaxial NW growth, including ZnO NW arrays.\(^{10,12,28,29}\) The extent of the buffer layer construction at the base of the NWs strongly depends on the magnitude of strain energy to be relieved, which is therefore a function of the lattice mismatch, the size of the NWs, and compound-dependent properties, along with other parameters.\(^{10}\) In systems with large lattice-mismatch and relatively large NW size, a conventional heteroepitaxial NW is expected to have a highly strained layer containing high density of defects even after the radial relaxation that might be experienced by the NW.\(^{5–10}\) Yet, as an interesting observation on our sample, both the heterointerfaces and the NWs were free from buffer layer, threading dislocations, and stacking defects.

To contrast our buffer layer- and threading dislocation-free growth of ZnO NWs on mica with previous theoretical and experimental data of buffer layer occurrence on ZnO NW array growth, we consider the size of our NWs which is typically 100–200 nm in diameter and 1.5–2 μm in length (Figure 1). It has been calculated that, assuming a strained epitaxy, heteroepitaxial NWs with diameter of 100 nm on 5% lattice-mismatched substrate can only grow to a critical height of around 0.8 nm before defects are nucleated.\(^{9}\) Besides, ZnO NWs on GaN substrate, which has only 2% lattice mismatch, had been shown to be limited to a maximum height of 2 nm for a defect-free growth when the NW diameter is 100 nm.\(^{10}\) Additionally, the growth of ZnO NW on a-sapphire substrate, which was inferred to have ~20% lattice mismatch, would always require growth of defective buffer layer at the base of the NWs. The above comparisons thus effectively highlight how a highly lattice-mismatched heteroepitaxial growth of defect-free NWs are enabled on muscovite mica substrate (−8.36% and 64.0% mismatch along two orthogonal zone axes) as reported herein. Absence of threading dislocations and buffer layer at the interface, despite the huge lattice mismatch, strongly suggest that the ZnO lattice is not excessively strained.\(^{9,10}\) Meanwhile, the average in-plane cell parameter of ZnO NW is preserved even after 20 nm away from the interface as measured from a strain mapping with Geometric Phase Analysis\(^{30}\) (Figure S5), signifying the absence of noticeable pseudomorphic and strained layers from the epitaxy. Therefore, we conclude that the epitaxy between ZnO NW–muscovite mica substrate could only be rationalized with vdWE, where our demonstration of heteroepitaxial growth of well-aligned NW array without buffer layer indicates the success of vdWE in circumventing the requirement of lattice matching with the substrate. While HRTEM of NW–substrate interface has been performed on vdWE-attributed InAs on graphite,\(^{31}\) the heteroepitaxy was concluded to be coherently strained and lattice matching-constrained. Our work is thus the first demonstration of incommensurate vdWE in nanowires, compatible with the general characteristics of vdWE in film growth.

Identification of atoms involved in the vdWE, that is, the atoms that are located in the surfaces of the contacting solids and thus responsible for the van der Waals interaction, is essential for the modeling of the epitaxy in order to construct the proper atomic arrangement at the interface\(^{25}\) (as shall be discussed in Figure 4). We thus study the polarity of the ZnO NW utilizing annular bright field scanning transmission electron microscopy (ABF-STEM) under aberration-corrected condition. The newly developed technique\(^{33}\) allows a direct imaging of the Zn–O dumbbells, which is found in the zigzag ABABAB stacking sequence along the length of the NW (Figure 3b), as expected of monocrystalline wurtzite structure.

In ABF imaging, darker contrast is attributable to the electron scattering from heavier elements. Hence, the brighter column of the dumbbell (Figure 3b,c), corresponding to a shallower dip in the intensity profile (Figure 3d), can be assigned to the position of O atoms. As the observed NW is oriented upright, with the conical tip located at the top of the NW (Figure 3a), we specifically assign that the growth direction of the ZnO NWs is along the positive c axis, which is indeed the fast growth
front in ZnO nanostructures, implying that the base of the NW is the O-terminated (0001̅) plane. To our knowledge, this is the first time that the polarity of as-dispersed NW is directly visualized from sample with light element (e.g., O and N) as a constituent of the dumbbell. Oxygen atoms are not resolvable under the well-established high angle annular dark field (HAADF) STEM (Figure S3), thus justifying the use of the novel ABF-STEM technique.

We further elucidate the properties of epitaxy by atomic 3D modeling of ZnO and mica. Using the experimental cell parameters, the model overlaps well with the atomic fringes of ZnO and muscovite mica when it is superimposed with the HRTEM image viewed from both of the zone axes (Figure 4a,c). In the evaluation of the heterointerface, we use the well-accepted potassium termination as the (001) cleavage plane of muscovite mica. Considering that the O atoms of ZnO are not resolved under HRTEM, the matching of the planes at the interface corresponds to the proximity between Zn atoms of ZnO and K atoms of mica. The periodicity of such proximity in our model is consistent to the results from Fourier-filtered HRTEM image (Figure 2b,d).

The sheet of muscovite mica is bound by a weak interlayer van der Waals force, which originates from the electric dipoles between the alternately stacked K⁺ layer and the negatively charged aluminosilicate layer. The bulk dipoles will remain on the surface of muscovite upon exfoliation, having a component pointing outward from the surface. Meanwhile, the difference in electronegativity of Zn and O atoms creates Zn²⁺ and O²⁻ ions, making the c plane in wurtzite ZnO polar. Consequently, the base of the NW also contains permanent electric dipole with component along the positive c axis. Thus, we hypothesize that the vdWE emanates from the permanent dipoles of ZnO and mica, with O²⁻ of ZnO and K⁺ of mica primarily being responsible for the dipolar attraction. We simulate the top view atomic arrangement of the first layer of Zn−O dumbbells of ZnO on the K atoms of mica (Figure 4e). Under this projection, maximization of van der Waals attraction is expected when a Zn atom coincides with a K atom with three O atoms surrounding them, as marked with a hexagon and rhombuses in the model. Hence, the net dipole moment of ZnO directly above the K atom is oriented vertically upward, and such sites would become the centers of anchoring for vdWE.

Although van der Waals forces are weaker than chemical bonds, we still expect the in-plane ZnO lattices to be slightly strained to allow the (1100)ZnO planes to reduce its mismatch, due to the more frequent proximity of O from ZnO and K atoms along [1120]ZnO||[010]Mica. Comparison of the experimental cell parameters of ZnO with its theoretical value (d_{(001)ZnO} = 0.2817 nm and d_{(020)Mica} = 0.16270 nm) revealed a minor deviation of around −0.6% in both in-plane directions under the definition of strain by \( \varepsilon = 100\% \times (d/d_t - 1) \). Association of the deviation as compressive strain is reasonable.
as the lattices in out-of-plane directions were expanded by 0.23% (experimental $d_{(0001)ZnO} = 0.5225$ nm, theoretical $d_{(0001)ZnO} = 0.5213$ nm), in good agreement with the theoretical expansion of around 0.21% due to Poisson’s effect ($\epsilon_{\text{out-of-plane}} \approx v \epsilon_{\text{in-plane}}$ where $v$ is the Poisson’s ratio of ZnO). Indeed, the $-0.92\%$ theoretical mismatch of (1100)ZnO to (200)Mica is higher in magnitude than that in our experimental result. Such adaptation of the ZnO lattices also confirmed that there exists a weak interaction across ZnO and mica, as was also suggested by the in-plane alignment of the NWs (Figure 1c inset), which we attributed as van der Waals-like instead of mere noninteracting deposit of atoms.

In conclusion, our results establish the characteristics of epitaxy in vdWE NW array, especially the capability of the lattices at the defect-free NW-substrate interface to feature incommensurateness. We believe that this possibility to achieve incommensurate epitaxy with vdWE might be one of the major reason for the successful growth of high crystalline quality NW arrays from various compounds on muscovite mica substrate (e.g., CdS, CdSe, CdTe, ZnTe, and PbS) regardless of their lattice mismatch. Such an encouraging results, combined with the vdWE characteristics in NW array as we established herein, suggest that the vdWE warrants further research attention to fully manifest its prospect in technology. For example, due to the irrelevance of lattice matching in vdWE, we believe that this possibility to achieve epitaxially. Hence, vdWE may facilitate studies of novel phenomena exhibited by such compounds and enable novel technological devices which require an epitaxial form of the compounds, especially those whose fascinating material properties were previously underexplored. Additionally, vdWE could also be utilized in the fabrication of integrated devices with multiple active materials, as it allows epitaxial growth of functional nanostructures from many different compounds within a substrate.

**REFERENCES**


**ASSOCIATED CONTENT**

Supporting Information
Materials and methods; detailed characterization of ZnO NWs; supplementary epitaxy analysis; additional images (Figure S1–S5). This material is available free of charge via the Internet at http://pubs.acs.org.

**AUTHOR INFORMATION**

Corresponding Author

*E-mail: arbiol@icrea.cat; Qijhua@ntu.edu.sg.

Notes
The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

Q.X. acknowledges the strong support from the Singapore National Research Foundation through NRF fellowship grant (NRF-RF2009-06), and from Nanyang Technological University through generous start-up grant support (MS8110061) and the New Initiative Fund (MS8110100). J.A. and F.J.B. acknowledge the funding from the Spanish MICINN projects MAT2010-15138 (COPEON) and CSD2009-00013 (IMAGINE) and Generalitat de Catalunya (2009 SGR 770, Nano-AraCat and XaRMAE). The authors thank the TEM facilities at the Universitat de Barcelona. We also acknowledge Rosa Córdoba at LMA-INA for help in the FIB sample preparation.


