Cadmium chalcogenides nanowire arrays on mica
Quantum transport in graphene nanonetworks
Plasmon enhanced solar-to-fuel energy conversion
Vertically Aligned Cadmium Chalcogenide Nanowire Arrays on Muscovite Mica: A Demonstration of Epitaxial Growth Strategy

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ABSTRACT: We report a strategy for achieving epitaxial, vertically aligned cadmium chalcogenide (CdS, CdSe, and CdTe) nanowire arrays utilizing van der Waals epitaxy with (001) muscovite mica substrate. The nanowires, grown from a vapor transport process, exhibited diameter uniformity throughout their length, sharp interface to the substrate, and positive correlation between diameter and length with preferential growth direction of [001] for the monocristalline wurzite CdS and CdSe nanowires, but of [111] for zinc blende CdTe nanowires, which also featured abundant twinning boundaries. Self-catalytic vapor–liquid–solid mechanism with hydrogen-assisted thermal evaporation is proposed to interpret the observations. Optical absorption from the as-grown CdSe nanowire arrays on mica at 10 K revealed intense first-order exciton absorption and its longitudinal optical phonon replica. A small Stokes shift (∼1.3 meV) was identified, suggesting the high quality of the nanowires. This study demonstrated the generality of van der Waals epitaxy for the growth of nanowire arrays and their potential applications in optical and energy related devices.

KEYWORDS: Nanowire array, muscovite mica, cadmium chalcogenides, van der Waals epitaxy, self-catalytic, excitonic states

During the past decade, nanowire arrays have been demonstrated for potentially wide applications ranging from lasing2 to solar cells2 to electrochemical applications.3 Nanowire arrays, especially those grown epitaxially, offer two significant advantages compared to randomly oriented nanowires: first, interfacial and bulky processes found in the conventional two-dimensional laminated-structured devices are decoupled such that either process can be efficient without compromising each other;5 second, certain electronic or photonic properties originated from individual nanowire associated with its orientation and directionality are amplified.1,4 In either case, it is imperative to accomplish epitaxial growth of nanowires. However, it is not trivial to achieve epitaxy and especially heteroepitaxy in nanowire array growth. Epitaxy requires that the lattice mismatch and the difference in thermal expansion coefficient be sufficiently small, which otherwise will hinder ordered growth due to accumulated strain. Therefore, previous syntheses of nanowire arrays were performed only with substrates possessing similar crystalline structures and small lattice mismatch with the materials of interest.

van der Waals epitaxy, a universal epitaxy strategy that has been proposed in film growth, aims to grow an epilayer onto a substrate without dangling bonds on its surface.5 In such a scenario, only van der Waals forces exist between the heterojunctions, causing the lattice matching condition to be relaxed dramatically. Despite the potential applicability of the strategy, van der Waals epitaxy in nanowire array growth has not been well documented.

In this study, muscovite mica is employed as the substrate for satisfying the condition of van der Waals epitaxy.6 It has easily cleaved layered structure having pseudohexagonal lattice with atomically smooth surface while being chemically inert, thermally stable, and commercially available. Considering these advantages, thin films of various materials have been epitaxially grown on mica7,8 which nonetheless have not been widely utilized due to the poor mechanical strength of mica. Although it is not an issue for nanowires as device fabrication can be separated from the growth by substrate transfer, reports of epitaxial growth of nanostructures on mica have been limited9−11 and the origin of the epitaxy has not been duly discussed.12

Meanwhile, among the materials explored in nanostructure growth, cadmium chalcogenides (CdS, CdSe, and CdTe), being...
important direct band gap II–VI semiconductors with quantum-confined size-tunable properties, have found ample utilization opportunities in nanophotonics. However, the vast majority of studies on cadmium chalcogenides were devoted to quantum dots while the syntheses of quasi-one-dimensional structures and arrays were reported only in the past few years. Cadmium chalcogenides are thus used herein to demonstrate the general applicability of mica in heteroepitaxial nanowire growth.

A freshly cleaved thin layer of muscovite mica (K₂O·3Al₂O₃·6SiO₂·2H₂O, research grade) was rinsed with acetone. Poly-L-lysine (0.1% w/v) was applied to the substrate for 5 min as it is found that this treatment significantly enhances the quality of the nanowire arrays grown. The substrate was then placed in the downstream region of a quartz tube on a single zone furnace (Lindberg/Blue M TF55035C-1) while the cadmium chalcogenide source in powder form (CdS: 99.9%, CdSe: 99.999%, CdTe: 99.99%) was positioned in the middle of the tube (Figure S1 in the Supporting Information). The system was evacuated to a base pressure of 2 mTorr, followed by a 30 sccm flow of high-purity Ar mixed with 5% H₂ gas before the system stabilized at the designated growth pressure. The system was set to 750 °C and 50 Torr for CdS, 775 °C and 50 Torr for CdSe, and 650 °C and 20 Torr for CdTe. In all cases, the system was elevated to the temperature in 10 min, to be maintained for 30 min, after which the system was allowed to cool to room temperature. The samples were thus collected and characterized by field-emission scanning electron microscopy (FESEM, JEOL JSM-7001F), X-ray powder diffraction (XRD, Bruker D8 advanced diffractometer, Cu Kα radiation), and transmission electron microscopy (TEM, JEOL JEM-1400 and JEM-2100).

The SEM images of the samples, given in Figure 1a–c, show that the cadmium chalcogenide nanowires were single-standing and highly oriented. We also obtained CdS vertically aligned low aspect ratio nanobelts, as shown in the upper inset of Figure 1a. Numerous CdS nanowires exhibited either clear hexagonal or triangular facets, while CdSe nanowires possessed an obtuse angled tip, and CdTe short nanowires/nanorods appeared to have a pyramidal tip with triangular cross section. Two mirrored faceting orientations of the CdTe wires to the substrate were noted, which is a strong indication of epitaxy, similar to the reported tetrahedra on sapphire substrates. Such structures were also obtained in growth trials with Au colloid nanoparticles or nickel nitrate salts dispersion on mica, suggesting that introduction of foreign catalyst species is unnecessary for the growth of arrays presented in this paper. The syntheses have been repeated multiple times, and these structures are reproducible. Growth trials away from the optimum condition of each nanowire growth, however, also resulted in a variety of structures such as tripods, tetrapods, sheets, and grains, all of which are still in nano- to micrometer scale.

The crystalline structure of the samples was identified by XRD, shown in Figure 1d, as wurtzite for CdS and CdSe while it was zinc blende for CdTe, which is in agreement with that of their respective bulk counterparts. The peaks from the muscovite mica was also found to be very intense, implying the high
crystallinity of the substrate. The (0002) peak from CdSe, pointed with solid arrow, is extremely strong and is about 140 times the intensity of (0004) peak, which is suggestive of the growth direction considering the high density of the nanowire array.

The morphology and crystallinity are further revealed from the high-resolution TEM given in Figure 2. High diameter uniformity over the whole length of nanowire was noted from the low magnification images. The nanostructures are generally single crystalline, as can be inspected from the clear selected-area electron diffraction (SAED) pattern, though exception occurs in CdTe where an appreciable number of wires exhibit twinning superlattice features. Two images of CdTe are hence presented: one with single crystallinity on the left and one showing the twinning on the right, where several of the defect locations are highlighted with hollow arrows along with an inset of the structure in lower magnification. The growth direction for CdS and CdSe nanowires were determined to be [0001] while that for CdTe were found to be [111], which are indeed the thermodynamically favorable growth direction for wurtzite and zinc blende structures, respectively. This may explain the occurrence of the twin plane defect in CdTe, which has been commonly observed in [111]-oriented nanowires, and its absence in CdS and CdSe whose c axis growth direction is fairly stable.

The [010] lattice spacing of mica (9.04 Å) is more than twice as large as the a axis of the 6-fold symmetric wurtzite CdS and CdSe and the (110) spacing family of cubic CdTe, all of which are to be arranged in the (001) surface of mica. Given the epitaxial relationship of (0001)_{CdS,CdSe}\parallel (001)_{mica} and (111)_{CdTe}\parallel (001)_{mica} we are to assume the orientation of the axes with the shorter lattice spacing direction of mica (5.19 Å) as the lower bound of the lattice mismatch of the heterojunctions, namely, [11\overline{2}0]\parallel [100]_{mica} for CdS and CdSe and [110]\parallel [100]_{mica} for CdTe. Nevertheless, lattice mismatches in those arrangements (~20.4% for CdS//mica, ~17.0% for CdSe//mica, and 13.7% for CdTe//mica) remain to be rather large and may thus be regarded as a demonstration of the general applicability of mica substrate in the growth of vertical nanowires via van der Waals epitaxy.

To the best of our knowledge, this is also the first report of vertically aligned single-standing monocrystalline low aspect ratio nanobelt from a bottom-up approach. The rectangular CdS nanobelts have a height in the range of 500–700 nm with a width of 300–500 nm and thickness of 40–70 nm, as measured from atomic force microscopy (AFM, Figure S2 in the Supporting Information). The belts may possess flat edges but a number of them own an uneven base and tip, as depicted in the insets of Figure 1a and 2a, which may be attributed to imperfect breaking of the interface with mica substrate during ultrasonication to prepare the TEM sample and incomplete growth, respectively. From SAED pattern, the growth direction of the belt is found as [11\overline{2}0]. The top and bottom surfaces are thus ±(1\overline{1}00) with ±(0001) side surfaces. This crystal facets assignment may explain the rectangular cross section of the belts and serve as a way to distinguish the CdS nanobelts from the (0001)-directed nanowires in TEM.

An important feature from the TEM images is the absence of metal catalyst at the tip of the nanowires characteristically found in a conventional vapor—liquid—solid (VLS) growth. Cross-sectional SEM images of the samples, shown in Figure 3, also show no structural disparity of the bottom part of the wires as compared to the remaining length of the wire. Instead, an abrupt interface with the substrate without buffer layer is exhibited, in
agreement with the clean facet of the nanowire base displayed in the TEM.

However, there are several evidences that are supportive for the nanowires to have experienced some form of catalyzed growth. First of all, the presence of directional growth of the nanowire itself, without noticeable tapering before the tip, for both the anisotropic wurtzite and the cubic zinc blende, which may require symmetry breaking. Second, the observation that the nanowires have relatively narrow diameter distribution, which has been shown to be controllable with catalyst seeds introduction or as a result of confinement from a seed particle. The diameter distribution of the CdS and CdSe nanowires measured from TEM images is shown in Figure 4, fitted with log-normal distribution function

\[ f(d) = f_0 + A \exp\left[-\left(\ln(d/d_0)/w\right)^2\right] \]

where \( f_0 \) is the baseline, \( d_0 \) is the most probable diameter, \( w \) is the peak width parameter, and \( A \) is a constant that describes the peak intensity) which has been previously utilized in the statistics of other nanomaterial growth.

Third, the findings that thick wires are generally longer than thinner ones, a phenomenon on VLS growth which has been discussed at length in various papers, in contrast to the result in other mechanism such as catalyst-free metal organic vapor phase epitaxy. A measurement of CdSe nanowire size distribution is also given in Figure 4 as the inset. Givargizov argued that the correlation between nanowire length and diameter is due to the dependence of nanowire growth rate on the supersaturation of the catalyst droplet as the driving force, which decreases in smaller diameter wires according to the Gibbs–Thomson effect. The explanation may also be applicable to the nanowires reported herein although a complication in the growth mechanism to be discussed, which inevitably affects the growth rate, did occur.

We hypothesize that the growth followed self-catalyzed mechanism. A process to produce Cd from cadmium chalcogenide powder has been reported by hydrogen-assisted thermal evaporation which can be generalized as

\[ \text{CdE}(s) + \text{H}_2 \xrightarrow{T} \text{Cd}(g) + \text{H}_2\text{E}(g) \]

where \( E = \text{S}, \text{Se}, \text{Te} \) and \( T \) is the temperature of the furnace during the synthesis. The Cd gas is thus transported downstream and condensed into liquid droplets on the substrate due to the driving force from the negative temperature gradient at the downstream region. The importance of hydrogen is emphasized as it was observed in the growth using high-purity Ar carrier gas that the nanowires are much less numerous, as it is nucleated only from Cd produced by the dissociation of the powder at high temperature due to the vapor pressure difference of Cd and the chalcogens, and much shorter. A larger area of film was also observed, although the evaporation was less rapid. On the contrary, it is noted that the deposition rate was considerably much faster when pure \( \text{H}_2 \) was used as the carrier. Most regions of the substrate were covered by a crystal layer although nanowires were also present, justifying the usage of mixed gas with Ar.

In the next step, the liquid Cd acts as a preferential adsorption site for CdE, which can be formed in the reverse reaction of the gaseous Cd and \( \text{H}_2\text{E} \) or progressive in situ conversion of the liquid Cd from exposure with \( \text{H}_2\text{E} \). An alloy of Cd and CdE is thus created while the adsorption proceeds, followed by nucleation and subsequent unidimensional crystallization which can occur in the liquid—solid interface once supersaturation is reached. In the meantime, the growth of single-standing nanowires can be understood as the interplay between the thermodynamics and kinetics of the growth. At low temperature, free diffusion of the adsorbed Cd species is inhibited by the atomic steps on the mica surface which serves as a diffusion barrier with a characteristic hierarchical energy, thus enabling the aggregation of isolated Cd droplets of certain shape and size to dictate the facet of the growing nanowires. However, at sufficiently higher temperature growth, the diffusivity might be high enough to overcome the barrier which may result in the growth of connected wall structures and crystal layers, if the deposition is also high (Figure S3 in the Supporting Information).

The angled tip formation in place of the metal catalyst presence has been reported in other self-catalyzed syntheses. The absence of a Cd-rich region on the wires was also strengthened by energy dispersive spectroscopy (EDS), which also showed that the Cd/chalcogenide atomic ratio is ~1:1 (Figure S4 in the Supporting Information).
atomically layered structure of mica. Meanwhile, the control of the nanowire length and diameter can be accomplished by appropriate positioning of the substrate, which will affect the substrate temperature and vapor supply consumption (Figure S5 in the Supporting Information). With this mechanism, contamination from a foreign metal catalyst commonly used in VLS growth is avoided.

Another interesting observation was that poly-L-lysine treatment on mica substrate prior to the growth improve the density of vertically aligned nanowires synthesized (Figure S6 in the Supporting Information). On untreated sample, more tilted wires were grown and the effective substrate area, hence the temperature range, containing good quality nanowires was much smaller. A similar advantage of lysine has been reported in the homoepitaxial vertically aligned growth on InP (001). It was suggested that crystalline ordering on the surface of InP substrate is hindered by lysine, whose residue still remains after high-temperature annealing, except the regions occupied by metal catalyst particle. Lysine has been used in studies mainly due to its ability to attach to nanoparticles, including metal catalyst of VLS growth, and thus opens the possibility of an identical role in conductor nanowires. The strong fundamental free exciton absorption and its phonon replica dominate the low-temperature spectra at wider energy range (Figure 6). A strong exciton peak was visible in the inset. The energy of ∼1.825 eV, is consistent with the first-order (n = 1) exciton, whose energy can be evaluated theoretically by

\[ E_{\text{ex}}(n) = E_g - \frac{R^*}{n^2} \]

where \( R^* = (\mu/m_e e^2) \times 13.6 \text{ eV} \) is the exciton Rydberg constant, with the band gap \( E_g \) of CdSe at 10 K being 1.84 eV, while its dielectric constant \( (\varepsilon_r) \) is 9.7 and reduced mass of exciton \( (\mu) \) is 0.1m_p with \( m_p \) being the rest mass of the electron. The exciton energy is also in good agreement with the values present in other works. One can see that the peak energy of FX_n is very close to the free exciton emission (FX_E), and the Stokes shift (\( A_{SS} \)) is

Figure 5. Room temperature absorption of CdSe nanowire arrays on mica and of pure mica substrate. CdSe nanowire arrays showed an absorption edge around 1.7 eV. Transmission spectra from mica with different thicknesses (right vertical axis) are also displayed. The strong interference effect identified in the vis−IR regime was associated to the atomically layered structure of mica.

Figure 6. The low temperature (10 K) free exciton emission and optical absorption of CdSe nanowires. Strong exciton absorption and its phonon replica were identified. The inset shows the absorption spectrum in a wider energy range, which clearly show sharp excitonic absorption superimposed on band edge absorption.
deduced to be only 1.3 meV, which is smaller compared to other published data.\textsuperscript{46,47} The presence of absorption and emission exciton peaks with small Stokes shift indicates the high quality and purity of the sample, which most probably was a result of the self-catalyzed growth and epitaxy mechanism. Another peak of absorption spectrum located at \(\sim 1.85\) eV can also be observed. The energy difference between this peak and FXA is \(\sim 26.7\) meV, which is in agreement with the longitudinal optical (LO) phonon energy of CdSe.\textsuperscript{48} Thus, this peak can be ascribed to the LO phonon replica of FXA and is denoted as FXA + 1LO.

In conclusion, a general strategy for achieving nanowire epitaxial growth from van der Waals epitaxy has been demonstrated by synthesizing vertically aligned nanowire arrays of cadmium chalcogenides on muscovite mica substrate, without the aid of foreign metal catalysts. The procedure allowed production of high-quality nanowires, to the point where the CdSe nanowires even exhibited exciton absorption peak and its phonon replica commonly observed only from the very high quality films. It is expected that the strategy offers wide opportunities for various optical and energy related applications based on vertical nanowire arrays, such as in nanowire photovoltaics where metal catalyst and impurities may introduce defect states and therefore limit device performance.\textsuperscript{49}

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