Video Article

Seedless Growth of Bismuth Nanowire Array via Vacuum Thermal Evaporation

Mingzhao Liu[1], Chang-Yong Nam[1], Lihua Zhang[1]

[1]Center for Functional Nanomaterials, Brookhaven National Laboratory

Correspondence to: Mingzhao Liu at mzliu@bnl.gov

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Abstract

Here a seedless and template-free technique is demonstrated to scalably grow bismuth nanowires, through thermal evaporation in high vacuum at RT. Conventionally reserved for the fabrication of metal thin films, thermal evaporation deposits bismuth into an array of vertical single crystalline nanowires over a flat thin film of vanadium held at RT, which is freshly deposited by magnetron sputtering or thermal evaporation. By controlling the temperature of the growth substrate the length and width of the nanowires can be tuned over a wide range. Responsible for this novel technique is a previously unknown nanowire growth mechanism that roots in the mild porosity of the vanadium thin film. Infiltrated into the vanadium pores, the bismuth domains (~ 1 nm) carry excessive surface energy that suppresses their melting point and continuously expels them out of the vanadium matrix to form nanowires. This discovery demonstrates the feasibility of scalable vapor phase synthesis of high purity nanomaterials without using any catalysts.

Video Link

The video component of this article can be found at https://www.jove.com/video/53396/

Introduction

Nanowires confine the transport of charge carriers and other quasiparticles, such as photons and plasmons in one dimension. Accordingly, nanowires usually exhibit novel electrical, magnetic, optical and chemical properties, which grant them nearly infinite potential for applications in micro/nano electronics, photonics, biomedical, environmental and energy-related technologies.[1,2] During the past two decades, numerous top-down and bottom-up approaches have been developed to synthesis a broad range of high quality metal or semiconductor nanowires at laboratory scale.[3-6] Despite of these developments, each approach relies on certain unique properties of the final product for its success. For instance, the popular vapor-liquid-solid (VLS) method is better fit for the semiconductor materials that have higher melting points and form eutectic alloy with corresponding catalytic "seeds".[7] As a result, the synthesis of a nanowire material of particular interest may not be covered by existing techniques.

As a semimetal with small indirect band overlap (-38 meV at 0 K) and unusually light charge carriers, bismuth is one such example. The material behaves radically different at reduced dimension when compared to its bulk, as quantum confinement could turn bismuth nanowires or thin films into a narrow band gap semiconductor.[8-12] In the meantime, the surface of bismuth forms a quasi-two-dimensional metal that is significantly more metallic than its bulk.[13,14] It was shown that the surface of bismuth achieves an electron mobility of 2×10^4 cm^2 V^{-1} sec^{-1} and contributes strongly to its thermoelectric power in nanowire form.[15] As such, there are significant interests on studying bismuth nanowires for electronic and in particular thermoelectric applications.[12-16] However, due to bismuth's very low melting point (544 K) and readiness for oxidation, it remains a challenge to synthesis high quality and single crystalline bismuth nanowires using traditional vapor phase or solution phase techniques.

Previously, it has been reported by a few groups that single crystalline bismuth nanowires grow at low yield during vacuum deposition of bismuth thin film, which is attributed to the release of stress built into the film.[17-20] Most recently, we discovered a novel technique that is based on the thermal evaporation of bismuth under high vacuum and leads to the scalable formation of single crystalline bismuth nanowires at high yield.[21] Comparing to previously reported methods, the most unique feature of this technique is that the growth substrate is freshly coated with a thin layer of nanoporous vanadium prior to bismuth deposition. During the latter's thermal evaporation, bismuth vapor infiltrates into the nanoporous structure of the vanadium film and condenses there as nanodomains. Since vanadium is not wetted by condensed bismuth, the infiltrated domains are subsequently expulsed from the vanadium matrix to release their surface energy. It is the continuous expulsion of the bismuth nanodomains that forms the vertical bismuth nanowires. Since the bismuth domains are only 1-2 nm in diameters, they are subject to significant melting point suppression, which makes them nearly molten at RT. As a result, the nanowires growth proceeds with the substrate held at RT. On the other hand, as the migration of the bismuth domains is thermally activated, the length and width of the nanowires can be tuned over a wide range by simply controlling the temperature of the growth substrate. This detailed video protocol is intended to help new practitioners in the field avoid various common problems associated with physical vapor deposition of thin films in a high vacuum, oxygen-free environment.

Protocol

Caution: Please consult all relevant material safety data sheets (MSDS) before use. Nanomaterials may have additional hazards compared to their bulk counterpart. Please use all appropriate safety practices when handling nanomaterial-covered substrates, including the use of engineering controls (fume hood) and personal protective equipment (safety glasses, gloves, lab coat, full length pants, closed-toe shoes).

1. Preparatory Work

1. Preparation of vapor deposition system
    1. Vent the deposition chamber to atmosphere pressure and open the chamber. The venting is done by pressing the "Start PC Venting" button on the control software interface, which automatically starts a sequence that vent the chamber to atmosphere pressure. On reaching the atmosphere pressure open the chamber by pulling the front accessing door.
    2. Mount a tungsten evaporation boat (alumina coated) between a pair of thermal evaporation electrodes. Place 1 g bismuth pellets into the evaporation boat.
    3. Mount a vanadium sputtering target to the magnetron sputtering source. Refer to step 1.1.4) for deposition system that is not equipped with a sputtering source.
    4. (*optional, for deposition system that is not equipped with a sputtering source*) Mount a tungsten evaporation boat between a pair of thermal evaporation electrodes. Place 0.5 g vanadium slugs into the evaporation boat.
    5. Connect the mini-banana connectors (two for heating/cooling power and two for temperature probe) of the closed loop temperature controller to the electrical feedthrough of the deposition system.

2. Preparation of growth substrates
    Note: The formation of bismuth nanowires is insensitive to the growth substrate of choice. Similar results have been obtained from glass slide, silicon wafer, or sheet metal. It is recommended by the authors that the substrate shall be cleaned immediately prior to the vapor deposition process, in order to achieve a consistent adhesion of the vanadium underlayer. Various substrate cleaning techniques, including plasma cleaning and wet chemical cleaning, can be applied and lead to similar results.
    1. Cleaning the growth substrates by oxygen plasma
        1. Place the growth substrates into a plasma cleaner and pump the chamber, by pressing the "VAC ON" button, to its base pressure of 10 mTorr.
        2. Open the oxygen gas valve and introduce oxygen gas to the chamber by pressing the "GAS ON" button on the front panel and adjust the flow rate by pressing the "INCR" and "DECR" buttons for gas flow rate control to maintain a chamber pressure of about 100 mTorr.
        3. Set the plasma power at 20 W by pressing the "INCR" and "DECR" buttons for power control and ignite the plasma by pressing the "RF ON" button.
        4. Wait for 5 min before turning off the plasma by pressing the "RF ON" button. Vent the chamber by pressing the "BLEED" button and retrieve the substrates.

    2. Cleaning the growth substrates by wet chemical method
        1. Immerse the growth substrates in acetone contained in a beaker. Place the beaker into an ultrasonicator and sonicate for 2 min at the maximum power.
        2. Remove the substrates from the beaker and rinse them with a stream of absolute alcohol from a wash bottle for 30 sec.
        3. Dry the substrates in a stream of nitrogen gas.

3. Substrate loading and deposition system pumping
    1. Mount the substrate temperature control assembly to the substrate holder.
    2. Use spring clips to mount the growth substrates on top of the Peltier cooler/heater assembly.
    3. Mount the fully assembled substrate holder into the vapor deposition chamber, with the substrates facing the deposition sources. Connect the electrical feedthroughs to the Peltier cooler/heater assembly.
    4. Close the substrate shutter to avoid unintentional deposition to the substrate.
    5. Start pumping down the deposition chamber. The pumping is done by pressing the "Start PC Pumping" button on the control software interface, which automatically starts a sequence that pump the chamber to its base pressure.

2. Growth of Bismuth Nanowires

Note: The experiment is not moving to the next step until the base pressure of the deposition chamber has reached 2×10^{-6} Torr or below.

1. The deposition of vanadium underlayer
    Note: The best experimental reproducibility is achieved when the vanadium underlayer is deposited by the magnetron sputtering method. In the absence of a sputtering source, high reproducibility can also be still achieved by depositing the vanadium underlayer using thermal evaporation method, provided that the deposition system has a low base pressure ($\leq 5 \times 10^{-7}$ Torr). Refer to step 3.1.2 for the details.
    1. Vanadium deposition with a magnetron sputtering source.
        1. Start argon flow in the sputtering source. Set flow rate to 40 sccm.
        2. Adjust the turbomolecular pump's revolution rate for a chamber pressure of 2.5 mTorr.
        3. While the chamber is gradually reaching its steady state pressure, set the thickness calibration factors to the QCM. For vanadium, the density is 5.96 g/cm^3 and the Z-factor is 0.530.

        4. Turn on the DC sputtering source and set the power at 200-250 W. For the deposition system operated by the authors, the deposition rate is about 0.4 A/sec at this power. Without opening the substrate shutter, keep the source running for 2 min. NOTE: Through this step the native oxide on the vanadium source is removed, exposing fresh vanadium surface.
        5. Open the substrate shutter to start vanadium deposition. In the meantime, reset the accumulated thickness of the QCM to zero.
        6. Continue deposition until an apparent thickness of 20 nm is accumulated, per QCM reading. Close the substrate shutter.
        7. Gradually decrease the sputter power to zero. Turn the source off.
        8. Shut off the argon flow. Return the turbomolecular pump to its full power.

    2. (*optional, for deposition system that is not equipped with a sputtering source*) Vanadium deposition with a thermal evaporation source.
        1. Due to the high melting point of vanadium (1,910 °C) and its readiness to oxidation, it is recommended that its thermal evaporation to be conducted at a base pressure of 5×10^{-7} Torr or lower.
        2. Set the thickness calibration factors to the QCM. For vanadium, the density is 5.96 g/cm^3 and the Z-factor is 0.530.
        3. Turn on the thermal evaporation power supply to the vanadium source. Slowly increase heating power to the tungsten boat until the vanadium slugs melt.
        4. With the substrate shutter kept closed, slowly increase heating power until a deposition rate of 2 Å/sec is achieved, per QCM reading. Open the substrate shutter to start vanadium deposition. In the meantime, reset the accumulated thickness of the QCM to zero.
        5. Continue deposition until an apparent thickness of 50 nm is accumulated. Close the substrate shutter.
        6. Gradually decrease the thermal evaporation power to zero. Turn the source off.

2. The deposition of bismuth nanowires
    1. For bismuth deposition at temperature above or below RT, set the desired value to the temperature controller. Wait until the desired temperature is reached.
    2. Set the thickness calibration factors to the QCM. For bismuth, the density is 9.78 g/cm^3 and the Z-factor is 0.790.
    3. Turn on the thermal evaporation power supply to the bismuth source. Slowly increase heating power to the tungsten boat until the deposition rate of 2 Å/sec is achieved, per QCM reading.
    4. Open the substrate shutter to start bismuth deposition. In the meantime, reset the accumulated thickness of the QCM to zero.
    5. Continue deposition until an apparent thickness of 50 nm is accumulated. Close the substrate shutter.
    6. Gradually decrease the thermal evaporation power to zero. Turn the source off.
    7. Turn off power supply to the thermal electric cooler/heater.
    8. Vent the deposition chamber to atmosphere pressure and open the chamber. Retrieve the substrate holder and collect the bismuth nanowires covered substrates.

Representative Results

The cross-sectional SEM images of vanadium underlayers formed by magnetron sputtering and thermal evaporation methods are presented in **Figure 2**. Scanning electron microscopy (SEM) images are presented for bismuth nanowires formed at different substrate temperatures (**Figure 3**). The crystal structure of the bismuth nanowires is determined through transmission electron microscopy (TEM), selective area electron diffraction (SAED), and X-ray diffraction (XRD) studies (**Figure 4**). Elemental analysis by energy dispersive X-ray spectroscopy indicates that the bismuth nanowires are not alloyed with the vanadium underlayer (**Figure 4**).

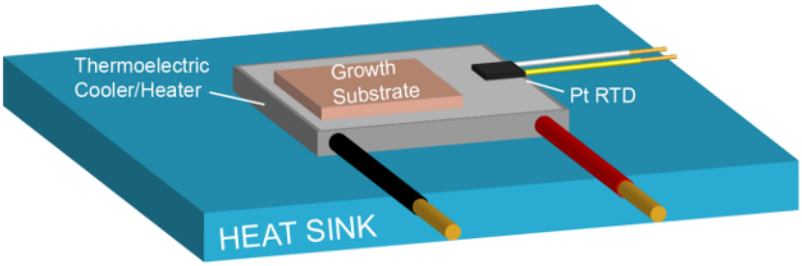

Figure 1. Layout of the substrate temperature control unit. The unit is assembled by thermally gluing a Peltier type thermoelectric module to a heat sink using silver filled epoxy. A platinum RTD is glued to the top (working) surface of the module to monitor the working temperature. The growth substrate is fixed to the top of the thermoelectric module by spring clips (not shown). Please click here to view a larger version of this figure.

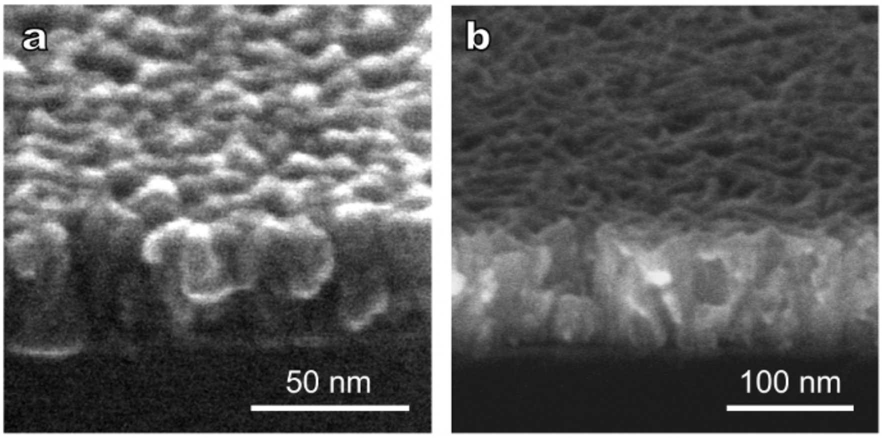

Figure 2. The SEM images of vanadium films freshly deposited over silicon substrate, respectively by magnetron sputtering (A) and thermal evaporation (B). As indicated by their vertical cross sections, both films feature a columnar and slightly porous structure. Please click here to view a larger version of this figure.

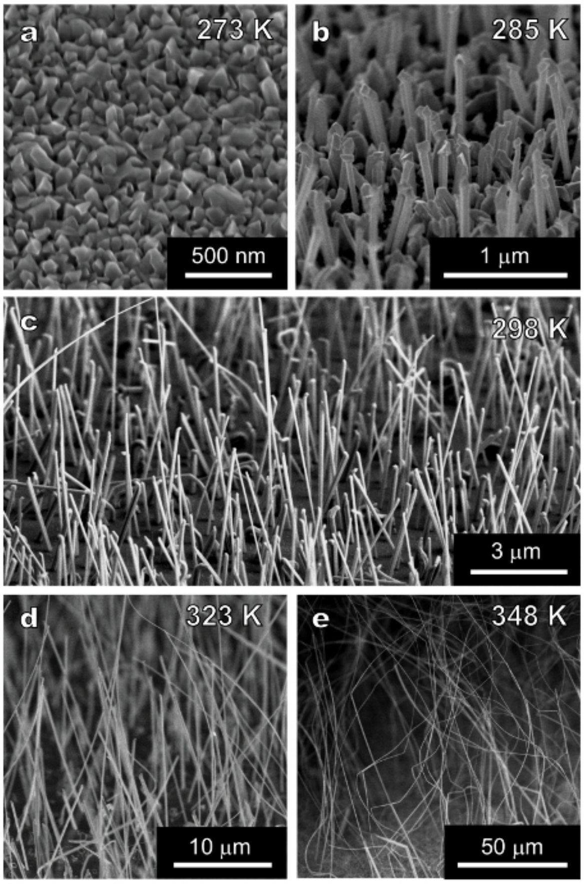

Figure 3. SEM images of bismuth deposits with the substrates held at different temperatures: (A) 273K, (B) 285 K, (C) 298 K, (D) 323 K, and (E) 348 K. Please click here to view a larger version of this figure.

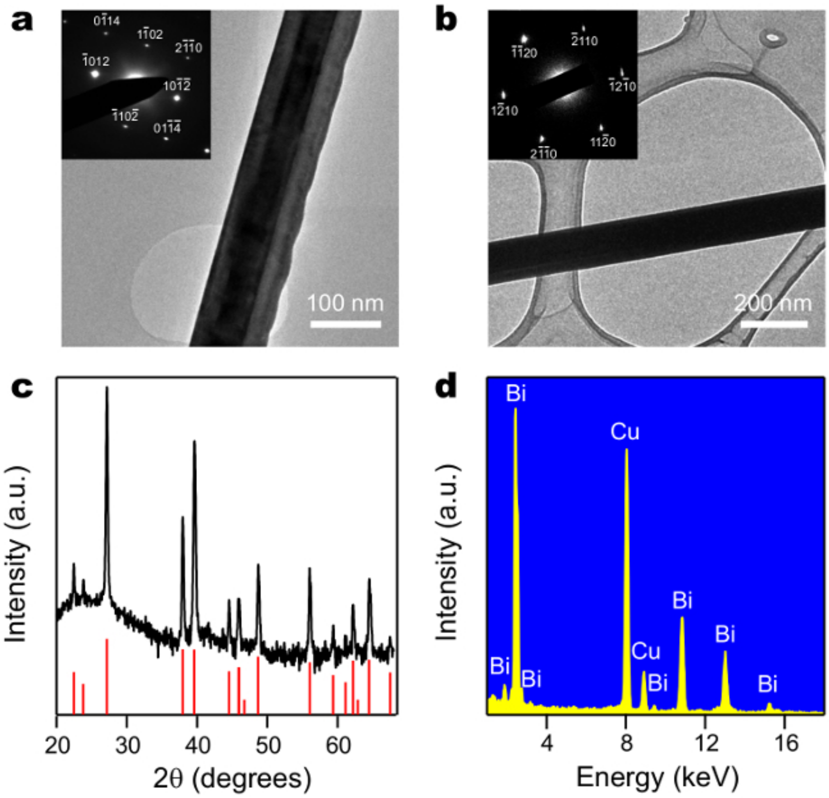

Figure 4. Characterization of the bismuth nanowires (A, B) transmission electron microscopy (TEM), (C) X-ray diffraction (XRD), and (D) energy dispersive X-ray (EDX) spectroscopy. The insets of panels (**A**) and (**B**) respectively show the corresponding selective area electron diffraction (SAED) patterns. In panel (**C**) the X-ray diffraction pattern of the bismuth nanowires is shown in black line, while the vertical red lines indicate the diffraction peak locations and intensities of bulk rhombohedral bismuth, according to its standard power diffraction file (PDF#01-071-4643). Please click here to view a larger version of this figure.

Discussion

The growth of bismuth nanowires is to be conducted in a physical vapor deposition system with at least two deposition sources, one for bismuth and another for vanadium. It is recommended that one of the sources is a magnetron sputtering source, for the deposition of vanadium. High vacuum is achieved by a turbomolecular pumps backed by a dry scroll pump. The vapor deposition system is equipped with a calibrated quartz crystal microbalance (QCM) for *in situ* thickness monitoring. The vapor deposition system has electrical feedthroughs for closed loop temperature control of the growth substrates. A thermoelectric temperature controller provides heating/cooling to the substrate, through a Peltier-type ceramic plate thermoelectric module that is thermally glued to a heat sink. Substrate temperature is monitored by a platinum resistance temperature detector (RTD). Refer to **Figure 1** for an illustration of the substrate temperature control unit.

Comparing to existing methods in literature, the present technique allows high yield (>70%) formation of single crystalline bismuth nanowires. The technique is also significant for its scalability: the amount of bismuth nanowires being deposited is only limited by the substrate size. For a successful growth of bismuth nanowires, it is critically important to deposit a nanoporous vanadium thin film that is consistently free of oxidation. Vanadium is chosen for its high melting point (1,910 °C), which makes it easy to form a porous film when deposited over a cold substrate. Other high melting metals, such as titanium (m.p. 1,668 °C), could promote bismuth nanowires growth in a similar fashion. Shown in **Figure 2** are the SEM images of vanadium thin films deposited by magnetron sputtering (a) and thermal evaporation (b) methods, which both show significant porosity. As discovered in our previous study, it is necessary for the infiltrated bismuth domains to be non-wetting to vanadium, so that they can be expelled from the porous vanadium matrix to form the nanowires.[21] An oxidized vanadium surface, however, is wetted by bismuth and cannot support nanowires growth. Considering vanadium's vulnerability toward oxidation, the experiment's success relies on how efficiently the spontaneous oxidation is prevented. It is found that the required consistency is best provided by magnetron sputtering under argon plasma. If thermal evaporation is the only choice for vanadium deposition, however, it is found that the required consistency is achieved when the base pressure is 5×10^{-7} Torr or lower. There are two contributing factors for the advantage of magnetron sputtering over thermal evaporation: 1) in magnetron sputtering the source is much cooler than the case of thermal evaporation, which slows down the oxidation; and 2) in magnetron sputtering the source is exposed to about 2 mTorr of argon flow, which suppresses oxygen partial pressure. In addition, the excessive radiative heat from thermal evaporation heats the deposition substrate very significantly, which makes it difficult to adjust the substrate temperature during the subsequent bismuth deposition, due to the limited power of the thermoelectric heater/cooler. If bismuth is deposited as a smooth and reflective film, it is due to the oxidation of vanadium film during its deposition. To avoid this from happening, the deposition chamber should be pumped for a longer time (such as O/N) to reach its base pressure.

As shown by the SEM images in **Figure 3**, the morphology of the bismuth deposits varies significantly at different substrate temperature. It is clear that at lowest temperature (273 K) no bismuth nanowire but a grainy film is deposited over the vanadium. Bismuth nanowires form at a substrate temperature as low as 285 K, but are thin (60-80 nm) and short (0.5-1 µm). At RT (298 K) the nanowires grow to 90-120 nm thick and 6-8 µm long. It is noticeable that the nanowire tips are faceted instead of being smoothly rounded, which is typically observed from VLS growth. The reason is that in this case the nanowire's growth front locates at the bismuth/vanadium interface, where the nanodomains of bismuth are molten. As soon as the molten bismuth erupts from the porous vanadium matrix, crystallization proceeds immediately to give the faceted appearance. The nanowires grow considerably thicker and longer at higher temperature. At 323 K, the nanowires are about 200 nm in diameter and 20-30 µm in length. At 348 K, the nanowires are about 400 nm in diameter and over 100 µm in length. Therefore, it is important to control the substrate temperature within a few Kelvins for consistent formation of bismuth nanowires of desired dimensions. Currently, the technique cannot be used to grow bismuth nanowires with diameter less than 60 nm. On the other hand, it seems that temperature control is not important during vanadium deposition, which is likely because that the substrate is always very cold when compared to the vanadium vapor.

The thermoelectric device illustrated in **Figure 1** is the solution for temperature control. With the heat sink held at RT, the substrate can be cooled to 273 K or heated to 373 K. Silver-filled epoxy is used for the thermal contact between the thermoelectric module and the heat sink. It is important that the epoxy is fully cured and dried of any solvent, since the vapor of the solvent may contaminate the substrate surface during vapor deposition and lead to inconsistent results. For the same reason no gel-like thermal paste should be used. Similar practice is made for the contact between the thermoelectric module and the Pt RTD.

In **Figure 4(a)(b)** we present the transmission electron microscopy (TEM) images of the bismuth nanowires. A survey of electron diffraction patterns (insets, **Figure 4(a)(b)**) reveals that most of the bismuth nanowires grow along either (1102) or (1210) directions. Despite not being a seed mediated growth such as the vapor-liquid-solid (VLS) mechanism, the bismuth nanowires are single crystalline, due to the presence of a growth front located near the bismuth/vanadium interface, where the liquid-to-solid phase transition happens. The nanowire's radial cross section could be irregular instead of circular, which leads to the darkness contrast observed in the TEM image shown in **Figure 4(a)**. Powder X-ray diffraction pattern (**Figure 4(c)**) also confirms that the bismuth nanowires crystalize in their bulk rhombohedral lattice (R3*m*). As indicated by the energy dispersive X-ray (EDX) analysis in **Figure 4(d)**, the nanowires are pure bismuth without alloying with vanadium (**Figure 4(d)**). The presence of signal from copper is due to the use of a copper TEM grid.

In summary, a novel technique is demonstrated in this article for scalable and high yield growth of single crystalline bismuth nanowires, induced by surface energy at bismuth/vanadium interface. The technique is capable of growing bismuth nanowires over a wide range of dimensions, simply by tuning the temperature of the growth substrate. It is anticipated that this simple but nontraditional growth mechanism will be further developed for the growth of other material system.

Disclosures

Authors have nothing to disclose.

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