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Surface-Energy Induced Formation of Single Crystalline Bismuth Nanowires over Vanadium Thin Film at Room Temperature

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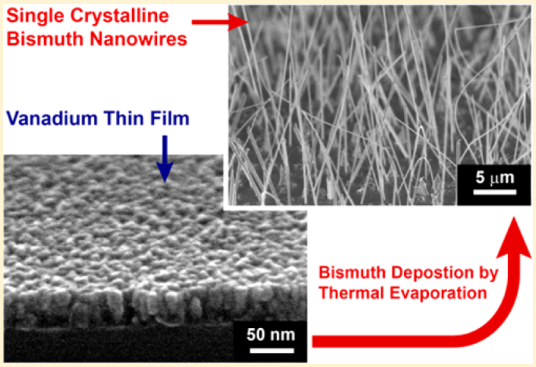
Supporting Information

ABSTRACT: We report high-yield room-temperature growth of vertical single-crystalline bismuth nanowire array by vacuum thermal evaporation of bismuth over a choice of arbitrary substrate coated with a thin interlayer of nanoporous vanadium. The nanowire growth is the result of spontaneous and continuous expulsion of nanometer-sized bismuth domains from the vanadium pores, driven by their excessive surface energy that suppresses the melting point of bismuth close to room temperature. The simplicity of the technique opens a new avenue for the growth of nanowire arrays of a variety of materials.



KEYWORDS: *Bismuth nanowire, single crystallinity, vanadium, thermal evaporation, surface energy*

As a semimetal with highly anisotropic Fermi surface and very light charge carriers ($\sim 10^{-3}$ m_e), bismuth has received much interest in recently years for its electronic properties as a Dirac Fermion gas.[1−3] Due to its low thermal conductivity (8.0 W m^{-1} K^{-1}) and carrier concentration ($\sim 10^{18}$ cm^{-3}), bismuth is a classic thermoelectric material that hosts Seebeck effect and Nernst-Ettingshausen effect. Electronic properties of bismuth evolve significantly when it is confined to nanoscale. On one hand, strong quantum confinement turns bismuth into a narrow band gap semiconductor.[4−6] On the other hand, charge transport at nanoscale is dominated by the surface states as the surface of bismuth is a quasi-two-dimensional metal with high mobility.[7,8] It is expected that the thermoelectric power improves significantly in bismuth nanowires, as the surface two-dimensional metal provides higher electrical conductivity while the phonon-surface scattering lowers the thermal conductivity.[8,9] The significant interests on studying bismuth nanowires for thermoelectric applications, however, are greatly hindered by the difficulty in scalable fabrication of high quality and single crystalline bismuth nanowires.[6−10]

The fabrication of bismuth nanowires usually relies on template-based methods such as pressure injection of molten bismuth into hard columnar templates, which inevitably introduces roughness to the nanowire surfaces.[6,11] Alternatively, stress-induced methods have been reported for the growth of bismuth nanowires free of templates.[12−14] In these methods, excessive stress is applied to bismuth lattice either by heating a bismuth thin film close to its bulk melting point or by forming a composite thin film with a material that has very different thermal expansion coefficient.[12−15] Although producing free-standing nanowires, these methods usually require precise control of substrate temperature and deposition condition for desired stress. The yield is also low as the nanowire growth stops once enough bismuth is "squeezed out" to eliminate the stress. In this Letter, we report a novel technique to scalably grow single crystalline bismuth nanowires in high yield, without using any seeds or templates. A key to this technique is a flat 20−40 nm thick vanadium thin film that is freshly deposited over a flat substrate maintained at room temperature, which can be glass, silicon, metal, or plastic. When bismuth is deposited over the vanadium thin film via thermal evaporation under high vacuum ($\leq 10^{-6}$ Torr), it is an array of single crystalline bismuth nanowires, rather than a flat bismuth thin film, that is formed. The deposition apparatus is illustrated in Figure 1a and the detailed deposition method is described in the Supporting Information.

The forest of out-of-plane nanowires covers the entire substrate (Figure 1b). As such, the deposited film is matte grayish rather than being mirror-like, which is normally expected from thermal evaporation of metal. The nanowires have smooth surfaces with diameters of 90−120 nm and lengths of 6−8 μm. It is confirmed by energy-dispersive X-ray spectroscopy (EDX) that the nanowires are pure bismuth

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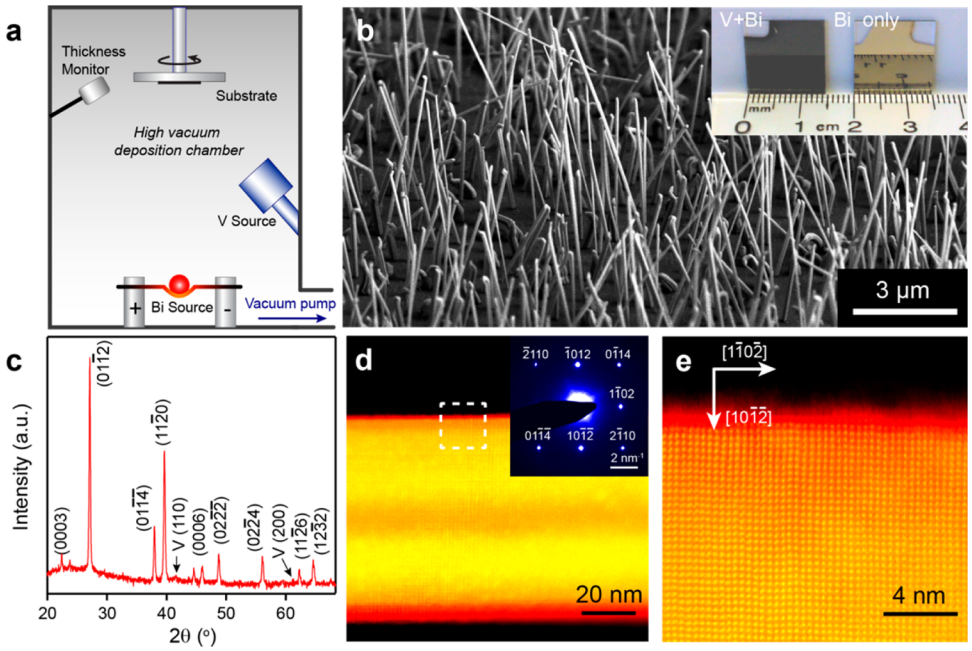

Figure 1. (a) The experimental apparatus for the sequential physical vapor deposition of elemental vanadium and bismuth, respectively, through magnetron sputtering and thermal evaporation. (b) SEM image showing the formation of out-of-plane nanowire array on the substrate during deposition, which appears matte grayish optically (inset, left). Bismuth thin film deposited without vanadium layer is mirror-like instead (inset, right). (c) XRD pattern recorded from the nanowire-covered substrate. The peaks are indexed according to the rhombohedral lattice of bismuth and *bcc* lattice of vanadium. (d) False color annular dark-field scanning TEM image of a bismuth nanowire that grows along $[1\bar{1}02]$ direction and the corresponding SAED pattern (inset). An area on the nanowire (enclosed by white dashed line) is imaged at atomic resolution (panel e), which confirms its single crystallinity and growth orientation.

without alloying with vanadium (Supporting Information, Figure S1). We estimate over 70% of the bismuth deposited on the substrate is converted to nanowires (Supporting Information, Figure S2). X-ray diffraction (XRD) pattern recorded from the as-deposited sample (Figure 1c) shows sharp peaks corresponding to rhombohedral bismuth. The diffraction peaks from vanadium (*bcc*, $2\theta = 42°$ (110) and 61° (200)), however, are only slightly above the background level due to its smaller grain size that gives substantial peak broadening. No other phases are observed, as bismuth and vanadium do not form solid solutions (Supporting Information, Figure S10).[16]

The presence of a freshly deposited vanadium layer is essential for the growth of bismuth nanowires. If the vanadium deposition is skipped, bismuth deposits as an optically smooth thin film despite an otherwise identical deposition condition (inset of Figure 1b and Supporting Information, Figure S3). The growth also exhibits strong dependence on the substrate temperature, which suggests it being thermally activated (Supporting Information, Figure S4). In our study, with the use of a Peltier substrate cooling/heating stage, the substrate is maintained at room temperature (295 K) during vanadium deposition while it is set to between 273 and 348 K during the bismuth deposition. We find that the higher substrate temperature increases the diameter and length of nanowires, respectively, to ~200 nm and 20−30 μm at 323 K, and to ~400 nm and over 100 μm at 348 K. On the other hand, when the substrate is cooled to 285 K, thinner (60−80 nm) and shorter (0.5−1 μm) nanowires are formed. At even lower substrate temperature (273 K), no nanowire growth is observed other than a continuous film.

The bismuth nanowires are mostly single crystalline with smooth surfaces. Presented in Figure 1d is an annular dark-field scanning transmission electron microscopy (STEM) image of a bismuth nanowire that extends along the $[1\bar{1}02]$ direction, as indicated by its selective area electron diffraction (SAED) pattern (for larger field-of-view on the same nanowire, refer to Supporting Information, Figure S5a). At higher magnification (Figure 1e), a nearly square lattice is revealed, as the $[1\bar{1}02]$ and $[10\bar{1}\bar{2}]$ directions can be respectively indexed as [100] and [010] in the pseudocubic notation for rhombohedral bismuth.[7] Further survey of the bismuth nanowires through TEM and SAED indicates that the most common growth directions are $[1\bar{1}02]$ and $[1\bar{2}10]$ (Supporting Information, Figure S5).

Thermal evaporation under high vacuum is a reliable method for depositing smooth and homogeneous metallic thin films, in which vaporized deposition material is transported from source to substrate in a ballistic fashion, following line-of-sight.[17] Although thin films can undergo surface reconstruction to form larger crystal domains, it is usually limited by high kinetic barrier and requires either elevated temperature or excessive stress to proceed. For example, it was reported that bismuth whiskers were formed during codeposition with high melting point metals or during magnetron sputtering over a heated substrate.[13−15,18] However, in our experiment, the substrate is maintained near room temperature (295 K), which is about 250 K below the melting point of bismuth. We estimate heating by the vapor and source radiation only lifts the temperature of top surface by less than 1 K at steady state (Supporting Information), thus indicating a very low kinetic barrier for the bismuth nanowire formation in our case, which is likely due to specific interaction at the vanadium/bismuth interface.

The sputter-deposited vanadium thin film appears flat but grainy under SEM, featuring a surface roughness of ~3 nm, while its vertical cross section clearly indicates a porous and columnar structure (Figure 2a). In the top-view TEM image, the vertical columns appear as individual islands separated by

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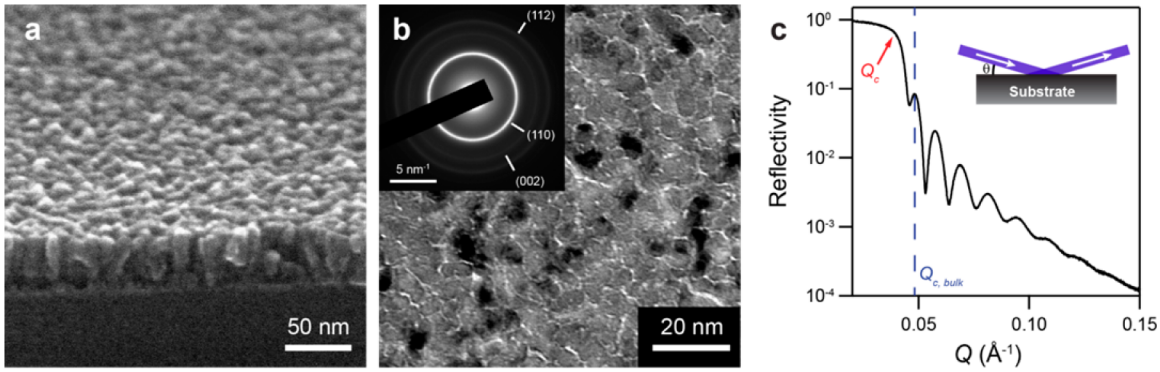

Figure 2. (a) The SEM image of an freshly deposited vanadium film over silicon substrate, featuring a surface roughness of 3−4 nm. The porous and columnar structure is clearly visible from its vertical cross section. (b) The top-view TEM image of an vanadium film deposited over a suspended SiO_2 window, in which the vanadium columns appear as discrete islands. Inset is the corresponding SAED pattern. (c) X-ray reflectivity R of the vanadium thin film is plotted against the momentum transfer vector Q. The critical moment Q_c is located and denoted by the red arrow. The dashed vertical line indicates the expected critical moment $Q_{c,bulk}$ for a vanadium film at its bulk density (6.0 g/cm^3). Inset shows the experimental geometry for reflectivity measurement.

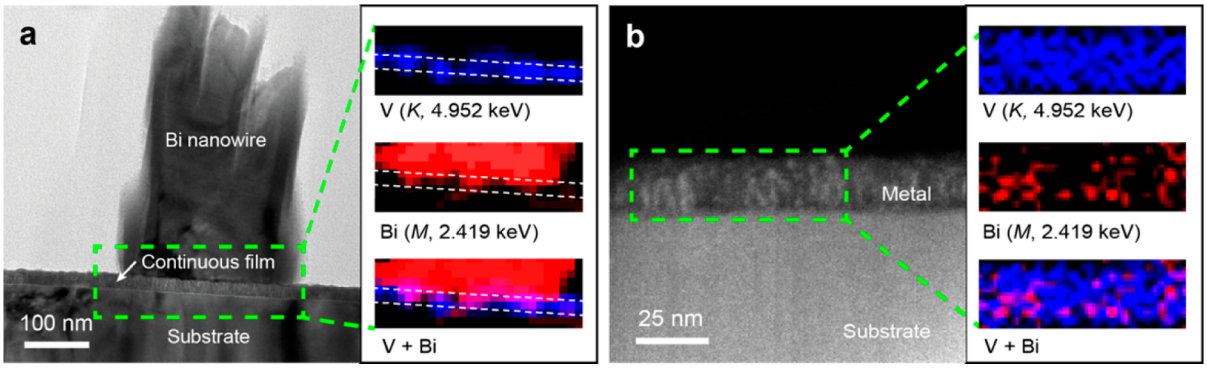

Figure 3. (a) Cross-sectional TEM image of an as-deposited bismuth nanowire over its growth substrate. The EDX mapping (right panel) indicates that the nanowire is pure bismuth (red) and that the continuous thin film is mostly vanadium (blue) but contains small amount of bismuth. The white dotted lines in EDX panel outline the location of the continuous film. (b) HAADF image of the continuous thin film and corresponding EDX mapping (right panel) reveal the inclusion of nanometer-sized bismuth domains into the vanadium thin film.

trenches of about 1 nm width, with the diameters 8−9 nm (Figure 2b). The SAED image confirms that the vanadium grains crystallize in bulk *bcc* lattice with no preferred orientation. The formation of a columnar thin film is typical during magnetron sputtering against a cold substrate, as the deposited atoms quickly lose kinetic energy before forming a closely packed structure.[19] The porosity of our vanadium film is quantitatively assessed through its X-ray reflectivity, which gives a direct measurement of the electron density profile in a thin film.[20,21] In Figure 2c, the reflectivity is plotted against the momentum transfer vector $Q = 4\pi \sin \theta/\lambda$, where θ is the incident angle and λ = 1.54 Å is the X-ray wavelength. The electron density ρ_e in the vanadium film is determined by the critical momentum Q_c, a value marked by the sudden decrease of reflectivity from near unity, through the relation $Q_c^2 = 16\pi r_e \rho_e$, in which $r_e = 2.818 \times 10^{-5}$ Å is the classical electron radius. We obtain ρ_e = 1.27 Å^{-3} based on the observed Q_c at 0.042 Å^{-1}, which is 78% of the electron density of bulk vanadium (1.63 Å^{-3}), thus suggesting a porosity of 22%. Should the vanadium film reach its bulk density, the critical momentum Q_c would be 0.048 Å^{-1}. Due to the interference between beams reflected from top and bottom surfaces of the vanadium film, Kiessig fringes appear at higher Q and are consistent with the film thickness of 40 nm (Supporting Information, Figure S6).[20]

As no nanowire is formed when bismuth is deposited over a *bulk* vanadium foil that is dense (Supporting Information, Figure S7), we believe the porosity of the sputter-deposited vanadium film is essential for the nanowires growth. During their vapor deposition in high vacuum, bismuth atoms can travel into the trenches between vanadium columns either directly or as adatoms through surface diffusion, before forming condensed domains, which potentially become nucleation centers for the nanowire growth. The low resolution cross-sectional TEM image (Figure 3a, left panel) reveals a continuous film over the substrate and a bismuth nanowire on top. The specimen is a 40 nm-thick cross-sectional slice of the bismuth/vanadium film mounted on a copper grid using the focused ion beam milling and lift-out technique, so only the base portion of nanowire remains in the slice. Through the EDX mapping, we confirm that the nanowire is pure bismuth and that the continuous film is mostly vanadium but contains small amount of bismuth (Figure 3a, right panel). At higher resolution, a high-angle annular dark-field (HAADF) image, which is highly sensitive to Z-contrast,[22] clearly shows brightness variation across the continuous thin film (Figure 3b, left panel), hinting the incorporation of bismuth (Z = 83) atoms into the vanadium (Z = 23) film. EDX mapping at higher resolution does locate scattered bismuth islands of 1−2 nm diameter (Figure 3(b), right panel) that correlate well with the

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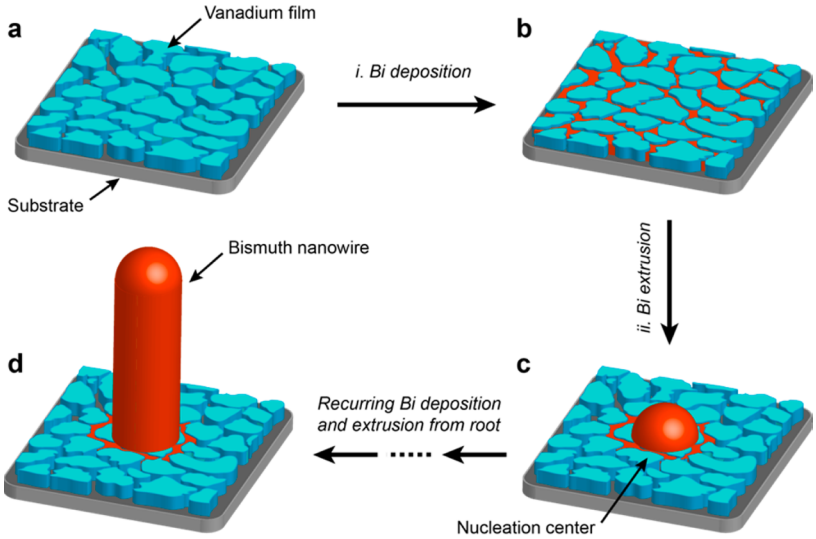

Figure 4. Growth of bismuth nanowires starts from the columnar vanadium film (a) being infiltrated by deposited bismuth (b). Next, the release of surface tension propels bismuth from the thin film, which forms a larger crystalline domain that serves as nucleation center for further growth (c). Finally, the continuous repeating of bismuth deposition and extrusion from the root of extruded domain leads to the growth of out-of-plane bismuth nanowire (d).

bright spots in the HAADF image. On the other hand, we do not observe any continuous bismuth layer on top of the vanadium-rich layer, which suggests that bismuth does not wet vanadium in its condensed form.

In a stress-induced mechanism, nanowire growth stops once the stress in the *bulk* is relieved. As a result, each nanowire is attached to a larger volume of "sprout" at its base,[12,14] with the conversion yield from the deposited material to nanowires limited to a few percent. However, in our case we show that over 70% of the deposited bismuth is converted to nanowires, which stand on the vanadium thin film with clean interface and absence of sprout-like structures (Figure 3a). A new mechanism for the nanowire formation is therefore proposed and illustrated in Figure 4. In this mechanism, bismuth vapor first infiltrates into the trenches between the vanadium columns and condenses there most likely as liquid phase with very large surface-to-volume ratio (step *i*). Driven by the excess surface energy, dispersed bismuth is immediately expelled from the trenches and agglomerates into a larger solid domain that serves as a nucleation center for future growth (step *ii*) and takes the shape of a nanoparticle to minimize the contact area with vanadium film, as bismuth does not wet vanadium. During its steady deposition, bismuth continuously flows to the bottom of the nucleation centers and crystallizes there to feed the one-dimensional extrusion, which eventually results in the formation of the out-of-plane single crystalline bismuth nanowires with the growth front at the root of a nanowire. This unique growth mechanism is a result of the highly directional and ballistic motion of the incoming bismuth atoms under high vacuum (Supporting Information). In this regime, most of the bismuth atoms can penetrate through the "forest" of nearly vertical bismuth nanowires and reach the bottom vanadium-rich film, where they are able to feed the axial growth of the nanowires. On the other hand, radial growth of the nanowires is suppressed as the nearly vertical nanowires bear very small cross sections to the incoming bismuth atoms from the source, despite that the nanowire side wall is a more energetically favorable position for adsorption of bismuth atoms. Such mechanism supports steady nanowire growth with continuous supply of bismuth, as long as the nanowires only shadow a small fraction of the growth substrate, thus producing nanowires of 20 μm or more in length. This process takes advantage of the more liquid-like surface of bismuth, which bears very large surface energy (0.55 N m^{-1} for solid phase and 0.375 N m^{-1} for liquid phase) and leads to significant melting point reduction for nanometer-sized domains.[23,24] In general, the melting point T_m of a small particle is related to its bulk melting point T_0 through

$$T_m/T_0 = 1 - \eta S/V \quad (1)$$

where η is related to surface energies of the solid and liquid phases and S/V is the surface area to volume ratio and is estimated to be 1.9 nm^{-1} for our case (Supporting Information, Figure S8).[24,25] Given the experimentally determined η = 0.23 nm,[25,26] we find an average local melting point T_m = 306 K, only ~56% of T_0, which indicates that the bismuth deposited into the vanadium trenches is near molten at room temperature, thus being highly mobile to migrate into larger crystal domains and eventually form the nanowires. Although mechanical stress lowers the melting point of bismuth due to its a denser liquid phase, the transformation of rhombohedral bismuth into denser solid phases at higher pressure sets its lowest melting point at 443 K at 2.13 GPa (Supporting Information, Figure S9), which remains significantly above room temperature.[27] It is therefore apparent that the nanowire growth at room temperature must be mainly attributed to surface energy, instead of stress.

The surface-energy-driven growth mechanism is consistent with the temperature dependence of nanowire growth. When the substrate is heated above room temperature, bismuth atoms on the substrate have surplus kinetic energy and diffuse further, yielding thicker and longer nanowires with lowered packing density. When the substrate is cooled, however, bismuth filled into the trenches freezes and cannot be expelled for the lack of mobility. Eventually, the trenches are completely filled and subsequent deposition of bismuth results in a continuous film.

A most direct and striking demonstration for the proposed growth mechanism can be realized by *in situ* high-resolution

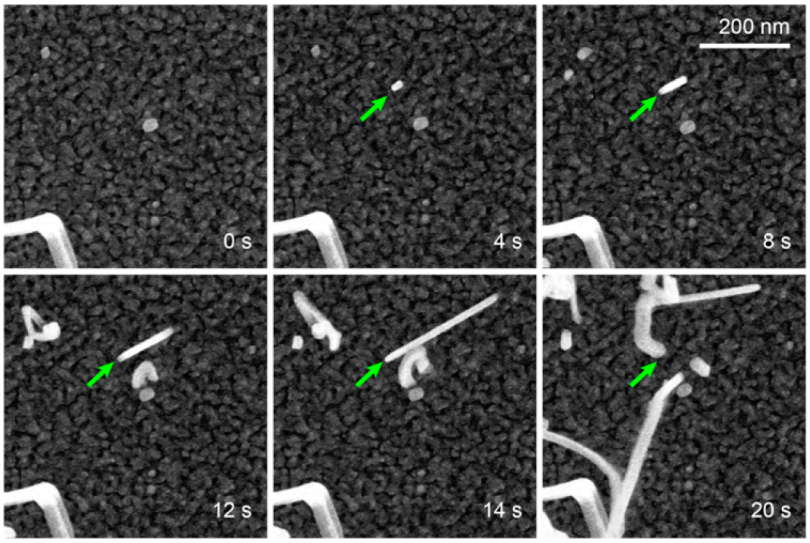

Figure 5. Bismuth nanowires grow *in situ* from as-deposited vanadium/bismuth film during high-resolution SEM study. The green arrows indicate the position of a nanowire growing continuously from a random spot on the film. As time elapses, increasingly more nanowires start to erupt from the area under electron beam scanning.

SEM studies, in which a subtle local heating induced by electron beam promotes more bismuth nanowire growth from as-deposited vanadium/bismuth nanowires thin films, without a bismuth evaporation source. For SEM studies, we choose an area located between preexisting bismuth nanowires and collect a sequence of SEM images from the same area during continuous electron beam scanning (Figure 5). The image features a grainy thin film at the beginning, but just in a few seconds of scanning a bright particle erupts from a random location in the scanned area and grows continuously into a nanowire. Later in the sequence, nanowires are seen to be erupting from multiple locations in this area. A real time SEM motion picture covering the *in situ* bismuth nanowire growth is available in the Supporting Information. We note the nanowires formed in this way are much thinner (10−20 nm in diameter), which reflects that the nanowire formation is now only fed by a limited supply of residual bismuth trapped between vanadium islands and that only the small area under electron beam scanning may contribute to the growth.

In summary, we discover that an array of out-of-plane, single crystalline bismuth nanowires are formed spontaneously and scalably during its vapor deposition through thermal evaporation in high vacuum. Unlike the traditional vapor−liquid−solid (VLS) mechanism,[28] in our case the formation of nanowires involves no apparent catalyst and follows a unique and novel mechanism. It is the nanoporous structure of the sputter-deposited vanadium thin film that confines the size of embedded bismuth domains during its vapor deposition, which causes an extraordinarily large surface-to-volume ratio and subsequent melting point reduction, rendering the bismuth domains molten or partially molten at room temperature. The release of surface energy provides the main driving force for the domains to diffuse and to finally erupt from the porous thin film to form nanowires. The technique is scalable as it is only limited by the size of the deposition substrate. Due to the universality of higher surface energy for nanoparticles, the mechanism we discover could become generally applicable for scalable growth of one-dimensional nanostructures of various other materials with moderate melting points. Furthermore, the absence of a catalyst in this method eliminates the unwanted but inevitable diffusion of catalyst atoms into the nanostructures,[29] thus enlightening a route for the scalable growth of nanostructure of higher purity and better controlled properties.

■ ASSOCIATED CONTENT

Supporting Information

Experimental methods for bismuth nanowires deposition and electron microscopy analysis; additional structural characterization of bismuth nanowires; real time video of *in situ* formation of bismuth nanowires in the SEM. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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