Functional Bimorph Composite Nanotapes

Rongrui He,† Matthew Law,† Rong Fan, Franklin Kim, and Peidong Yang*

Department of Chemistry, Materials Science Division, Lawrence Berkeley National Laboratory, University of California, Berkeley, California 94720

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ABSTRACT

Single-crystalline nanoribbons were used as substrates for the epitaxial growth of different functional thin films deposited by laser ablation techniques. This simple method yields highly crystalline bilayer nanotapes with sharp structural and compositional interfaces. As an example, Co0.05Ti0.95O2@SnO2 nanotapes are shown to be ferromagnetic at room temperature. These composite nanotapes, with their various possible functionalities, represent an important new class of nanoscale building blocks for optoelectronic applications.

This synthetic method yields high aspect ratio (i.e., 100−2000) single-crystalline nanoribbons with {101} growth directions and well-faceted, nearly rectangular cross-sections bounded by {101} and {010} surface planes (Figures 1b,c).9 The crystalline perfection and atomically flat surface facets of these nanoribbons make them excellent substrates for the epitaxial growth of materials with appropriate crystal symmetries. The good thermal stability of these oxide nanoribbons is equally important to their versatility as substrates because they can survive the harsh conditions required for many conceivable vapor deposition processes.

Electron microscopy and X-ray diffraction studies clearly demonstrate that these functional oxides grow epitaxially on the side surfaces of the substrate nanoribbons with sharp structural and compositional interfaces, and so form a unique class of bilayer nanoribbons (Figure 1a) with significantly enhanced functionality. As an example, the Co0.05Ti0.95O2@SnO2 nanotapes are shown to be ferromagnetic at room temperature.

The rutile SnO2 nanoribbons used in this study were synthesized according to previously reported procedures.9

* Corresponding author. E-mail: p_yang@uclink.berkeley.edu.
† These authors contributed equally to this work.

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The overall ribbon morphology is maintained after the deposition, and the average nanoribbon thickness increases (Figure 1d). X-ray diffraction taken on the resulting nanotapes (Figure 1e) shows two sets of diffraction peaks corresponding to the rutile SnO2 and TiO2 structures, with no other phases present.

Structural and compositional analysis was carried out on these samples to characterize the TiO2@SnO2 interface. Figure 3a shows a TEM image of a single composite nanotape, revealing its clean and sharp laminated morphology. It was found that the thin film coating on the nanoribbon is essentially single crystalline. The epitaxial nature of the interface was further characterized by HRTEM in detail. The TiO2 deposition results in an atomically sharp interface between TiO2 and SnO2, as shown in Figure 3b. This particular nanotape has the TiO2 epitaxially oriented on the narrow side (010) surface. The different lattice spacings for the two (010) planes of the rutile TiO2 and SnO2 structures (4.64 Å vs 4.84 Å) can be well resolved in Figure 3b. The electron diffractions taken on the two sides of the interface (insets in Figure 3b) further demonstrate that an excellent epitaxial relationship is established between the TiO2 and SnO2. In addition, Figure 3c presents a line profile of the elemental composition perpendicular to the tape axis, which also confirms the formation of an anisotropic bilayer nanotape structure with a smooth interface and external surface.

Importantly, a cross-sectional TEM image taken on a nanotape (Figure 3d) unambiguously reveals the quasi-rectangular bilayer morphology of the nanotape. Electron diffraction at the interface again shows only two sets of well-correlated diffraction patterns that indicate the excellent interfacial epitaxial relationship between the two materials.
except for this particular nanotape, the TiO$_2$ is epitaxially grown on the wide side (01$\bar{1}$h) plane. The energetic nature of the laser ablation process makes the plume highly directional and enables the selective film deposition on one side of the nanoribbon substrate due to the shadow effect. The epitaxy observed in these TiO$_2$@SnO$_2$ nanotapes is reasonable considering the relatively small lattice mismatch (2.9% for $a$ and 7.0% for $c$) between the TiO$_2$ and SnO$_2$ rutile structures. Interfacial stress, however, does exist in these bimorph structures as seen in the TEM studies.

The same PLD approach was used to deposit Co-doped TiO$_2$ thin-films on the SnO$_2$ nanoribbons in an effort to synthesize ferromagnetic semiconducting nanotapes. Figure 4 shows a series of TEM images of one such Co$_{0.05}$Ti$_{0.95}$O$_2$@SnO$_2$ structure. The highly crystalline nature of the entire ~5 $\mu$m long nanotape, with its abrupt interface, smooth and uniform coating, can be readily seen here. Similarly, transition metal doped ZnO (e.g., Mn$_{0.1}$Zn$_{0.9}$O, Ni$_{0.1}$Zn$_{0.9}$O) has been successfully deposited on ZnO nanowires/ribbons to form homo-junctioned ZnO nanotapes. Importantly, we clearly observed ferromagnetic ordering at room temperature for the Co-doped rutile composite tape samples. Figure 5 shows magnetization (M) data as a function of the applied field (H) for a Co$_{0.05}$Ti$_{0.95}$O$_2$@SnO$_2$ nanotape sample. It must be emphasized that the formation of other phases CoTiO$_3$, CoTi$_2$O$_5$, Co, and CoO has not been observed in any of our electron microscopy and X-ray diffraction studies, probably due to the nature of nanoscale epitaxial growth in our process.

The methodology reported here is highly versatile, and we focus on the TiO$_2$@SnO$_2$ nanotape system only as a showcase introduction to this powerful synthetic approach. It should be possible to fabricate highly crystalline nanotapes or core–sheath structures of many other complex materials using different metal oxide nanoribbons (ZnO, MgO, Al$_2$O$_3$) as substrates. Important features of this nanoribbon-based approach to lateral heterostructure formation reside in its flexibility in materials choice, synthetic simplicity, and high-quality epitaxial structures, which differ significantly from previously reported core–sheath structures. Possible nanotape functionalities are essentially unlimited, and could readily include luminescent, ferro-

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**Figures:**

Figure 3. (a) TEM image of a TiO$_2$@SnO$_2$ nanotape; inset is its low magnification image. (b) HRTEM image of the atomically sharp TiO$_2$@SnO$_2$ interface. 4.64 and 4.84 Å correspond to the lattice spacing between the (010) planes in TiO$_2$ and SnO$_2$ rutile structures. Insets are electron diffractions taken on the two sides of the interface along the same [102] zone axes. (c) Compositional line profile across the TiO$_2$@SnO$_2$ interface as outlined in (a) (from A to B). (e) Selected area electron diffraction pattern recorded at the cross section area in (d). The SnO$_2$ and TiO$_2$ layers are in the same zone axis and have the same orientation, indicating perfect epitaxy.

Figure 4. TEM images of a ~5 $\mu$m long Co$_{0.05}$Ti$_{0.95}$O$_2$@SnO$_2$ nanotape produced by PLD. Images (b–e) were taken on this individual nanotape as shown in (a), areas (1–4), respectively. (f) Electron diffraction pattern recorded at the interface. These structures were synthesized by ablating a Co$_{0.05}$Ti$_{0.95}$O$_2$ target at 700 °C in 125 mTorr of O$_2$ using laser ablation parameters similar to those described in Figure 1.

Figure 5. An M–H curve for a Co$_{0.05}$Ti$_{0.95}$O$_2$@SnO$_2$ nanotape sample taken at room temperature. The data were recorded using a superconducting quantum interference device magnetometer (Quantum Design MPMS).
magnetic (transition metal doped TiO$_2$ and ZnO, LaMnO$_3$), ferroelectric (BaTiO$_3$, PbTiO$_3$), and superconducting (YBa$_2$Cu$_3$O$_y$) properties. These composite bimorph nanotapes represent a novel class of highly functional, one-dimensional nanoscale building blocks for nanowire-based devices.

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