Preparation and Field Emission Properties of Titanium Polysulfide Nanobelt Films

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ABSTRACT

TiS₃ nanobelt films, with widths of about 0.1–12 μm, thickness of about 20–250 nm, and lengths of up to 200 μm, have been grown on Ti substrates by a surface-assisted chemical-vapor-transport at 450 °C for 8 h. The TiS₃ nanobelt films were converted into TiS_{1.71} nanobelt films by pyrolysis in a vacuum at 600 °C for 2 h. The work functions of the two films were determined by ultraviolet photoelectron spectroscopy measurements to be 4.60 and 4.44 eV, respectively. Preliminary field emission experiments using the nanostructures as cold electron cathodes showed that both materials gave significant emission currents. The turn-on fields (defined as the electric field required to produce a current density of 10 μA/cm²) were about 1.0 and 0.9 V/μm, respectively, whereas the threshold fields (defined as the electric field required to produce a current density of 1 mA/cm²) were about 5.6 and 4.0 V/μm, respectively. These data reveal that both materials have potential applications in field emission devices.

KEYWORDS

Nanowire, film, titanium sulfide, chemical vapor-transport, field emission

Introduction

One-dimensional (1-D) nanomaterials have attracted considerable interest due to their unique physical properties and potential applications in the construction of nanoscale electric and optoelectronic devices [1–6]. A few 1-D nanomaterials have already been synthesized and fabricated into devices [7–10], but for future rational development and optimization of functional devices it is important to synthesize novel 1-D nanostructures and to understand their fundamental physical properties.

Titanium trisulfide (TiS₃) is an n-type extrinsic semiconductor with good conductivity. It has a pseudo one-dimensional structure with infinite chains of triangular prisms (TiS₆) that share trigonal faces along the *b*-axis. Each chain is shifted with respect to two neighboring ones by half the lattice parameter along the *b* direction [11]. Titanium disulfide (TiS₂) exhibits either semimetallic [12] or semiconducting [13] behavior due to a strong tendency toward nonstoichiometry with excess Ti. Over the past few years, TiS₃ and TiS₂ thin films have been prepared by chemical vapor deposition (CVD) of TiCl₄ and a series

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of sulfur sources [14], and TiS_3 nanobelts have been prepared by a chemical vapor transport (CVT) of Ti sponge and S powder [15]. In addition, TiS_2 nanotubes have been prepared by the thermal decomposition of TiS_3 in H_2 at 800–1000 °C [16], and by heating TiS_2 amorphous particles in H_2 at 200 °C [17]. If 1-D nanostructures of TiS_3 or TiS_2 are fabricated on metal or semiconducting substrates, they can form electronic field emission (FE) functional blocks due to the strong local electric field at the tip and unique direction of electron emission. Earlier, Zhang et al. prepared TiS_2 whisker arrays on Si substrates by a vapor deposition method, but no physical properties were studied [18]. We also fabricated TiS_2 microplates on Ti substrates by surface-assisted CVT [19], but did not obtain any 1-D nanostructures. Here we report that by altering the previous experimental conditions, it is possible to obtain TiS_3 nanobelt films on Ti foils, and that the TiS_3 nanobelt films can be pyrolyzed in a vacuum to afford $\text{TiS}_{1.71}$ nanobelt films. We also report FE measurements with both films.

1. Experimental

Titanium (Ti) foil (99.9%) and sulfur (S) powder (99.8%) were used as starting materials. Three pieces of Ti foil with size of ca. 0.2 mm × 5 mm × 11 mm (total weight: 136.0 mg) and S powder (10.0 mg) were sealed in a quartz ampule (Φ 6 mm × 130 mm) under a vacuum (ca. 10^{-2} Pa). The ampule was placed in a conventional horizontal furnace with a temperature gradient of ca. 10 K/cm from center to edge. The end containing the Ti foil was put at the center of the furnace, and the ampule then heated at different temperatures (350, 450, 550, and 650 °C) for 8 h; finally TiS_3 nanobelt arrays grown on Ti foil were obtained. After the furnace was cooled to room temperature, the pieces of foil with attached TiS_3 nanostructures were extracted from the quartz ampule. The product obtained at 450 °C was sealed in a quartz ampule (Φ 6 mm × 250 mm) under a vacuum (ca. 10^{-2} Pa). The end of the ampule containing the TiS_3 nanostructure was put at the center of the furnace, with the other end extending out of the furnace by about 7 cm, and the ampule was then annealed at 600 °C for 2 h in a vacuum so as to obtain $\text{TiS}_{1.71}$ nanobelt films.

The products were characterized using an X-ray diffractometer (XRD; Shimadzu XRD-6000) with graphite monochromatized Cu $K\alpha$ -radiation, a scanning electron microscope (SEM; LEO-1530VP) with attached energy-dispersive X-ray spectrometer (EDX), and a high-resolution transmission electron microscope with a point resolution of 0.19 nm (HRTEM; JEOL model JEM-2100). The composition of the products was confirmed by a gravimetric method: the products scraped from the Ti foils were weighed, and converted to TiO_2 by heating in air at 800 °C for 1 h, and then cooled to room temperature. The atomic ratios of Ti and S were calculated based on the weight loss of the products. The work functions were measured by ultraviolet photoelectron spectroscopy (UPS, ESCALAB 250) with an ultraviolet excitation source (He I discharge at $h\nu = 21.22$ eV) in a vacuum of 3×10^{-8} Pa. The spectrum was recorded with a sample bias of −3.500 V so that the sample inelastic cutoff could be distinguished from that of the spectrometer. The electron field emission measurements were performed by using a parallel-plate configuration with a space of 500 μm and an emission area of 0.41 cm^2 in a vacuum chamber at a pressure of 5.0×10^{-4} Pa at room temperature. A DC voltage sweeping from 0 to 4500 V was applied to the samples.

2. Results and discussion

2.1 Structure and morphology

Figures 1(a)–(d) show the XRD patterns of the films prepared by reaction of Ti foil with S at different temperatures. Figure 1(a) indicates the reflection peaks of the product obtained at 350 °C, which can be indexed as the hexagonal phase of Ti (ICCD PDF no. 05-0682), revealing that Ti does not react with S below 350 °C. Figures 1(b) and 1(c) exhibit the reflection peaks of the nanostructures prepared at 450 and 550 °C, respectively, which can be indexed as the monoclinic phase of TiS_3 (ICCD PDF no. 36-1337; S. G.: $P2_1/m$). Figure 1(d) displays the reflection peaks of the product obtained at 650 °C, which can be indexed as the hexagonal phase of TiS_2 (ICCD PDF no. 15-0853). After the films prepared at 450 °C were

annealed in a vacuum at 600 °C for 2 h, they were converted to hexagonal $\text{TiS}_{1.71}$, for which the XRD pattern is shown in Fig. 1(e) (ICCD PDF no. 71-0374; S. G.: $R\bar{3}m$).

Figures 2(a)–(c) are SEM images of the TiS_3 nanobelt films obtained at 450 °C, which show that the nanobelts, with widths of about 0.1–12 μm , thickness of about 20–250 nm, and lengths of up to 200 μm , were vertically or obliquely grown on the Ti substrate. The EDX spectrum (Fig. 2(d)) gave a the molar ratio of Ti to S of 24.2:75.8 (1:3.13), which is close to the expected stoichiometric composition. In addition, gravimetric analysis gave almost the same Ti/S molar ratio, 1:3.10. Figures 2(e)–(g) show a high-magnification TEM image, a selected area electron diffraction (SAED) pattern, and an HRTEM image of a single TiS_3 nanobelt, respectively. The SAED pattern can be indexed as TiS_3 (ICCD PDF no. 36-1337), consistent with the above XRD results. Lattice fringe spaces of 0.49 and 0.34 nm correspond to (100) and (010) planes of TiS_3 , which demonstrate that the nanobelt grows along the [010] direction. The structure of the nanobelt

is drawn as an inset in Fig. 2(g).

Figures 3(a)–(c) are SEM images of the nanobelt films obtained at 550 °C, showing that the nanobelts, with widths of about 0.4–17 μm , thickness of about 50–300 nm, and lengths of up to 440 μm , grew almost vertically on the Ti substrate. EDX and XRD analyses demonstrate that the material is also TiS_3 (ICCD PDF no. 36-1337). When the reaction was carried out at 650 °C, only TiS_2 particle films were formed as shown in Fig. 3(d).

Figures 4(a)–(c) are the SEM images of $\text{TiS}_{1.71}$ nanobelt films with sizes and morphologies which approach those of the TiS_3 nanobelt precursors prepared at 450 °C. The EDX spectrum (Fig. 4(d)) confirms that the nanobelt is composed of Ti and S with a molar ratio of 36.95:63.05 (1:1.71). Gravimetric analysis shows that Ti/S molar ratio of the products is 1:1.76, consistent with the EDX analysis. Figure 4(e) shows a TEM image and corresponding SAED pattern (inset) of a single $\text{TiS}_{1.71}$ nanobelt. The SAED analysis supports the above XRD results and confirms that the nanobelt grows along the [100]

Figure 1 XRD patterns of the films prepared at (a) 350, (b) 450, (c) 550, and (d) 650 °C, and (e) $\text{TiS}_{1.71}$ nanobelt film formed by pyrolysis of a TiS_3 nanobelt film (prepared at 450 °C) in vacuum at 600 °C

Figure 2 (a) Low-magnification plan-view; (b) high-magnification plan-view; (c) low-magnification side-view SEM images of a TiS_3 nanobelt film prepared at 450 °C; (d) EDX spectrum of TiS_3 nanobelts. (e) TEM image; (f) SAED pattern; (g) HRTEM image of a single TiS_3 nanobelt

Figure 3 (a) Low-magnification plan-view; (b) high-magnification plan-view; (c) low-magnification side-view SEM images of a TiS_3 nanobelt film prepared at 550 °C; (d) plan-view SEM image of a TiS_2 particle film prepared at 650 °C

Figure 4 (a) Low-magnification plan-view; (b) high-magnification plan-view; (c) low-magnification side-view SEM images of a $\text{TiS}_{1.71}$ nanobelt film prepared by vacuum pyrolysis of a TiS_3 nanobelt film (obtained at 450 °C); (d) EDX spectrum of $\text{TiS}_{1.71}$ nanobelts; (e) TEM image and corresponding SAED pattern (inset) of a single $\text{TiS}_{1.71}$ nanobelt; (f) HRTEM image and corresponding SAED pattern (inset) of a single $\text{TiS}_{1.71}$ nanobelt

direction. Figure 4(f) shows an HRTEM image and SAED pattern (inset) of a single $\text{TiS}_{1.71}$ nanobelt. The lattice fringe space of 0.21 nm corresponds to the (0016) plane of $\text{TiS}_{1.71}$.

2.2 Growth mechanism

Tips of nanobelts can be observed in Fig. 3(b) which suggests that the formation of TiS_3 nanobelts can be explained by the vapor–solid growth mechanism [20]. When the reaction temperature reaches 450 °C, sulfur (b.p. 444.6 °C) is evaporated into the vapor phase, and deposits on the Ti substrate. Titanium reacts with sulfur vapor and forms unstable TiS_x species in the gas phase. TiS_x in the vapor phase reacts with further S vapor, and condenses again on the Ti substrate to form stable TiS_3 seeds. In the subsequent process, TiS_x and S in the vapor phase may combine with TiS_3 seeds to form TiS_3 nanobelts. Owing to the presence of the seeds, TiS_3 nanobelts stand almost vertically on the surface of the substrates, similar to the growth of MoO_2 nanorod arrays on Si substrates [21]. When the reaction proceeds at 650 °C, TiS_3 seeds are decomposed into TiS_2 particles resulting in films of TiS_2 . Compared with our previous experiments [19], we think that the reaction time influences the stoichiometries and morphologies of the products formed.

2.3 UPS analysis

Work functions of the materials were measured in ultrahigh vacuum using the inelastic secondary electron cutoff of UPS energy distribution curves [22]. Before the spectra were recorded, the surfaces of the samples were cleaned by Ar^+ sputtering with an applied energy of 2 keV and a beam density of 0.5 $\mu\text{A}/\text{mm}^2$ for 200 s. After a high purity Ni plate was sputtered, its UPS spectrum on the kinetic energy scale was recorded as shown in Fig. 5(a), and

the spectrometer was calibrated by the Fermi edge of Ni. The spectrum width from the Fermi edge to the sample inelastic cutoff, as determined by the centers of the slopes (Fig. 5(a)), is equal to $h\nu - \Phi$ (where $h\nu$ is the photon energy and Φ is the work function) [22]; the work function of Ni was confirmed as 4.01 eV. The UPS spectra of TiS_3 and $\text{TiS}_{1.71}$ are shown in Figs. 5(b) and 5(c), respectively. The positions of the sample inelastic cutoff for TiS_3 and $\text{TiS}_{1.71}$ correspond to values of the work functions of 4.60 and 4.44 eV, respectively (although the Fermi edge is not observed, the value can be taken as the same as that for Ni, since the Fermi edge is the reference point of the energy scale in UPS and should not change from sample to sample as long as they are grounded [22]).

Figure 5 UPS spectra of (a) Ni plate, (b) TiS_3 nanobelt film, and (c) $\text{TiS}_{1.71}$ nanobelt film.

2.4 Electronic field emission

The emission current–voltage characteristics were analyzed by using the Fowler–Nordheim (F–N) equation for the field emission: $J = (AE^2 \beta^2 / \Phi) \cdot \exp[-B\Phi^{3/2} / (E\beta)]$, where J is the current density (A/m^2), E is the applied field, $B = 6.83 \times 10^9 \text{ (eV}^{-3/2} \text{V} \cdot \text{m}^{-1})$, $A = 1.56 \times 10^{-10} \text{ (AV}^{-2} \cdot \text{eV)}$, β is a field enhancement factor, and Φ is the work function [23]. Figures 6 (a) and 6(b) depict the curves of the emission current density (J) as a function of applied field (E) of the TiS_3 nanobelt films obtained at 450 °C and the $\text{TiS}_{1.71}$ nanobelt films, respectively, and insets show the corresponding F–N plots, that is, the plots of $\ln(J/E^2)$ versus $1/E$. The F–N plots exhibit an approximately linear behavior in the low field region but nonlinear behavior in the high field region, which may result from space charge effects in the vacuum space [24]. Based on the J – E curves, we can determine the field emission turn-on fields and threshold fields, which are defined as the macroscopic fields required to produce a current density of $10 \text{ } \mu\text{A}/\text{cm}^2$ and $1 \text{ mA}/\text{cm}^2$, respectively. The turn-on fields of TiS_3 and $\text{TiS}_{1.71}$ are 1.0 and 0.9 $\text{V}/\mu\text{m}$, respectively, and the threshold fields are 5.6 and 4.0 $\text{V}/\mu\text{m}$, respectively. Based on the work functions of TiS_3 (4.60 eV) and $\text{TiS}_{1.71}$ (4.44 eV) determined as above, and the slopes of the F–N plots, field enhancement factors of the TiS_3 and $\text{TiS}_{1.71}$ nanobelt films are calculated as $\sim 1.63 \times 10^4$ and $\sim 2.14 \times 10^4$, respectively. Both turn-on fields and threshold fields are comparable to the values reported for Mo (2.2 and 6.24 $\text{V}/\mu\text{m}$) [21], AlN (3.8 and 7 $\text{V}/\mu\text{m}$) [25], and ZrS_2 (0.95 and 3.6 $\text{V}/\mu\text{m}$) nanowire arrays [26]. Therefore, both nanostructures are candidates for future field emitters. Because the $\text{TiS}_{1.71}$ nanobelt films were prepared by vacuum pyrolysis of the TiS_3 nanobelt films, the amounts (per cm^2) and morphologies of the two nanostructures are very similar. Therefore, the FE performances of the materials depend strongly on their work function. It should be noted that the work function measured here is an average over the emitting material and the local work function at the tips of individual 1-D nanostructures, where most electrons are emitted, has an important effect on the FE properties [27, 28]. The maximal emission current of the $\text{TiS}_{1.71}$ nanobelt

arrays is greater than that of the TiS_3 nanobelt arrays, which may be attributed to the greater stability of the $\text{TiS}_{1.71}$ nanobelts. Emission stabilities of the $\text{TiS}_{1.71}$ nanobelt films were tested at a constant electric field

of $7.0 \text{ V}/\mu\text{m}$. As shown in Fig. 7, the initial current and the average current densities were 3.14 and $3.03 \text{ mA}/\text{cm}^2$, respectively, and no obvious degradation of current densities was observed after 4 h.

Figure 6 Current density–electric field curves for (a) TiS_3 nanobelt films obtained at 450°C and (b) $\text{TiS}_{1.71}$ nanobelt films obtained by vacuum pyrolysis of the above TiS_3 nanobelt films at 600°C for 2 h. Insets are the corresponding F–N plots

Figure 7 Emission current density vs. time curves for $\text{TiS}_{1.71}$ nanobelt films at $7.0 \text{ V}/\mu\text{m}$

3. Conclusions

TiS_3 nanobelt films have been fabricated on Ti substrates by a facile surface-assisted chemical-vapor-transport approach. The morphologies and structures strongly depend on the reaction conditions including quantities of reagents, reaction temperature, and reaction time. TiS_3 nanobelt films can be decomposed to give $\text{TiS}_{1.71}$ nanobelt films by vacuum pyrolysis. Both films possess low turn-on fields and high field enhancement factors. These properties could make the nanobelt film ensembles highly valuable for use in novel FE nanodevices.

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