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ABSTRACT
Thin tellurium (Te) has been predicted as a potential two dimensional system exhibiting superior thermoelectric and electrical properties. Here, we report the synthesis of high quality ultrathin Te nanostructures and the study of their electrical properties at room temperature. High quality ultrathin Te nanostructures are obtained by high temperature vapor phase deposition on c-plane sapphire substrates. The obtained nanostructures are as thin as 3 nm and exhibit α-Te phase with trigonal crystal structure. Room temperature electrical measurements show significantly higher electrical conductivity compared to prior reports of Te in bulk form or in nanostructure form synthesized by low temperature vapor deposition or wet chemical methods. Additionally, these nanostructures exhibit high field effect hole mobility comparable to black phosphorous measured previously under similar conditions.

Tellurium (Te) is an elementary semiconductor predicted to exhibit striking physical properties in thin nanostructures such as extraordinarily high hole mobility, high thermoelectric performance, outstanding gate electrostatics, few interface traps, and dangling bond-free interfaces. Te exhibits a tunable bandgap as a function of thickness, from nearly direct 0.33 eV in the bulk to indirect 0.92 eV in monolayer. The trigonal crystal structure of Te consists of 1D helical chains of Te atoms stacked together on a 2D hexagonal lattice. The atomic distance between two neighboring Te atoms along the chain is 2.9 Å, whereas the atomic distance across the chains is 3.9 Å. Each Te atom is covalently bonded with its two nearest neighbors on the same chain, while the atoms on the nearest helical chains are weakly bonded and the weak bond is assumed to be van der Waals type or covalentlike quasibonding. Because of its unique crystal structure, nanostructures of Te can be synthesized as one-dimensional (1D) as well as two-dimensional (2D) nanostructures.

It has been recently reported that monolayer and multilayers of Te can potentially exist in a stable 1T-MoS₂-like (α-Te) structure, as well as the metastable tetragonal (β-Te) and 2H-MoS₂-like (γ-Te) structures. The α- and γ-Te can thus be considered as transition metal dichalcogenides of general formula MX₂ (X = S, Te, Se) in which transition metal (M) has been replaced by Te. While the β-Te is the more stable phase for the monolayer, the α-Te is the preferred phase at normal pressure for layers thicker than one monolayer. Additionally, α-Te shows excellent environmental stability compared to other 2D materials such as black phosphorous (BP). Thin α-Te is, therefore, a candidate material for thermoelectric, electronic, optoelectronic, and piezoelectric applications as its physical properties are predicted to compete with other novel layered materials such as BP and MoS₂.

Te nanostructures in 1D and 2D forms have been previously synthesized by solution-based methods, low temperature vapor phase deposition methods, and exfoliation of bulk Te. However, high temperature vapor phase methods are generally preferred for growing higher crystal quality material and would be a desirable approach to create high quality Te nanostructures. However, the high evaporation rate of Te at high temperature makes this challenging due to re-evaporation of deposited Te nanostructures kept at high temperature. A novel approach is required to mitigate this problem. Here, we report high temperature synthesis of ultrathin Te nanostructures by vapor phase deposition. Using ZrTe₂ as a source material and carefully controlling the substrate and source position to overcome the aforementioned challenge, we obtained high quality, ultrathin Te nanostructures that have thicknesses as low as...
3 nm. The electrical properties were investigated at room temperature (RT). These Te nanostructures exhibited an order of magnitude lower resistivity compared to bulk Te. Furthermore, we observed high hole mobility which is comparable to the hole mobility of BP at room temperature.

The ultrathin Te nanostructures were synthesized by vapor phase deposition in a tube furnace. A schematic of the tube furnace experimental setup is shown in Fig. 1(a). Initial synthesis attempts were made by using Te powder (American Elements, 99.999% purity) as a source material, which was kept in an alumina boat, and a growth substrate (sapphire), which was placed either on the downstream of the Ar flow or face-down directly on the top of the alumina boat. The growth substrate was either bare or coated with ~3 nm thick gold or nickel films. As our aim was to grow Te nanostructures at high temperature, the temperature of the growth substrate was maintained at ≥ 600 °C for all the experiments. The alumina boat with Te source was placed at various temperature zones to control the Te evaporation when the substrate was placed downstream. The Te source and the substrate were at the same temperature zone when the substrate was kept on the top of the source boat. The growth resulted in a granular thick film as shown in Fig. 1(b) when the growth substrate was placed on the aluminum boat over the source or no growth with the metal nanoparticle catalyst as shown in Fig. 1(c) when the substrate was placed downstream of the Ar flow. A possible reason for this observation could be the high evaporation rate of Te, at ≥ 600 °C, making it challenging to control the necessary growth condition. ZrTe₂ as an alternative Te source material was thus used to mitigate this problem. It is known that ZrTe₂ decomposes into gaseous Te and crystalline Zr when heated at sufficiently high temperature. The decomposition of ZrTe₂ is a slow process; therefore, it can potentially allow improved control of the evaporation rate of Te at higher temperatures, whereas Zr remains crystallized on the source boat. Under a stable growth condition, the distribution of Te species is determined by the balance of evaporation, diffusion, and convection rates. Diffusion, being a slow process, provides more uniform distribution of Te species and enables desirable conditions to nucleate nanostructures on the growth surface. The dominant convection transport of Te species at a high evaporation rate is more likely to result in a granular film. ZrTe₂ powder as a Te source is expected to limit the Te evaporation and provide adequate balance of diffusion and convection transport of Te species to grow nanostructures at high temperature. ZrTe₂ powder (American Elements, 99.99% purity) was placed into an alumina boat and a c-plane sapphire growth substrate was placed face-down on the top of the boat. In a typical synthesis process, several purge cycles were first conducted to remove oxygen and moisture in the quartz tube. Ar gas was supplied as the carrier gas, and the pressure was maintained at 150 Torr. The temperature of the furnace was then ramped up to 750 °C at the boat location, and the temperature was maintained for 30 min.

The morphology of the resulting Te nanostructures grown using ZrTe₂ powder was characterized by scanning electron microscopy (SEM) and atomic force microscopy (AFM). Figure 1(c) shows an SEM image of the sapphire substrate following growth, exhibiting nanowirelike Te nanostructures oriented randomly with respect to the sapphire. The length of these nanostructures varies from a few hundred nanometers to a few microns, and the width varies from tens of nanometers to a few hundred nanometers. The nanostructures were examined using AFM to estimate their thickness distribution. An AFM image of the nanostructures as-grown on the sapphire surface is shown in Fig. 2(a). Figure 2(b) presents the histogram plot of the nanostructure thickness distribution, demonstrating thickness variation from few nanometers to ~30 nm. For example, the thickness of a nanostructure crossed by the green line in Fig. 2(a) was measured to be ~3.2 nm. If the thickness of the monolayer of Te is ~0.391 Å, the 3.2 nm thick nanostructure contains about 8 layers of Te.

The crystallography of the nanostructures was investigated by scanning transmission electron microscopy (STEM). Nanostructures were transferred directly from the growth sample to a TEM grid by scraping the sapphire substrate and dispersing the materials on the TEM grid. Additionally, cross sections of the Te nanostructures for STEM study were prepared by focused ion beam (FIB) milling of the as-grown nanostructures on the sapphire substrate. The STEM measurements were conducted using an FEI Themis Z instrument operated at 300 keV and an FEI Titan instrument.
Although ZrTe EDS maps are shown in Figs. 3(e)–3(h). It is important to note that by energy dispersive x-ray spectroscopy (EDS) analysis in the STEM.

The Te nanostructure in Fig. 3(a) is single crystalline as evident from the STEM HAADF image, and the nanostructure has its longer axis oriented along the c-axis. Figure 3(d) shows the cross-section of the Te nanostructure obtained from AFM measurements.

Fourier transform (FFT) pattern from the image [Fig. 3(b)] is shown has been overlaid on Fig. 3(b), which perfectly matches the structure in Fig. 3(a). The image was taken in the [100] zone, with lattice planes (0,1.0), (0,1,1), and (0,0,3) as indicated. The nanostructure has a trigonal crystal structure with hexagonal cell, space group P3121, and lattice parameters \( a = 4.458 \) Å and \( c = 5.927 \) Å. The observed crystallographic structure is consistent with the α-Te phase. A projected lattice structure along [100] for the α-Te phase has been overlaid on Fig. 3(b), which perfectly matches the structure obtained from the HAADF STEM image. Furthermore, the fast Fourier transform (FFT) pattern from the image [Fig. 3(b)] is shown in Fig. 3(c), and its indexing is consistent with the trigonal phase of α-Te. The nanostructure in Fig. 3(a) is single crystalline as evident from the STEM HAADF image, and the nanostructure has its longer axis oriented along the c-axis. Figure 3(d) shows the cross-sectional STEM image of a Te nanostructure on the sapphire substrate, where the bright region represents the cross section of the Te nanostructure.

The chemical composition of the nanostructures was studied by energy dispersive x-ray spectroscopy (EDS) analysis in the STEM. EDS maps are shown in Figs. 3(e)–3(h). It is important to note that although ZrTe2 powder was used as a source material to enable high temperature Te nanostructures synthesis, we did not see any trace of Zr in the nanostructure to the detection limit of the EDS measurement [Fig. 3(b)].

Room temperature electrical measurements of single-Te nanostructure devices were carried out to investigate their electrical properties. For the electrical measurements, Te nanostructures were transferred to a Si/SiO2 substrate and devices were fabricated with Ti/Au contacts on the Te nanostructures by electron beam lithography (EBL). Figure 4(a) shows I-V characteristics of a Te nanostructure device. Upper and lower insets of Fig. 4(a) are SEM and AFM images of the device, respectively. In the presented device, the length of the nanostructure channel is \(~830\) nm, the nanostructure width is \(~180\) nm, and the thickness is \(~21\) nm. From the I-V measurement, the resistivity \( (\rho) \) of the Te nanostructure is estimated to be \( 64.5 \) \( \mu\Omega \) m. Specifically, this obtained resistivity is significantly lower than the reported resistivity of bulk-Te. Moreover, the room temperature resistivity of these Te nanostructures is significantly lower than the resistivity of solution-based synthesized Te nanostructures, suggesting that the high temperature synthesis can indeed produce superior quality Te nanostructures.

The electrical properties of the Te nanostructure were further investigated by measuring the current through the nanostructure \( (I_\alpha) \) as a function of gate voltage \( (V_g) \) in a field effect transistor (FET)-like configuration. Gate voltage was applied on the nanostructure through the underlying SiO2 layer (bottom gate configuration). The transfer characteristics of the Te nanostructure FET device are shown in Fig. 3(b). The negative slope of the \( I_\alpha-V_g \) curve indicates that the majority charge carriers are holes. Recent detailed band structure calculations of Te have revealed that a unique structure of the valence band at the H point in the Brillouin zone provides conduction channels for the holes. The fourfold degenerate valence band at the H point is split into two nondegenerate H4 and H5 bands and a doubly degenerate lower H6 band due to the strong spin-orbit coupling in the Te. Both the H4 and H5 bands lie close to the Fermi level and thus contribute to holes transport, whereas the H6 band lies at a lower energy position and does not significantly contribute holes to the conduction.

Field effect hole mobility and concentration were estimated from the \( I_\alpha-V_g \) data using the following equations: \( \mu_h = \frac{g_m L^2}{V_d C_{get}} \) and \( n_h = \frac{1}{e \mu_h} \), where \( \mu_h \) is the field effect hole mobility, \( g_m = \frac{dI_\alpha}{dV_g} \) is the transconductance, \( C_{get} \) is the gate capacitance, and \( e \) is the electronic charge. For a flat nanostructure, the gate capacitance can be obtained by a simple parallel plate approximation, given by \( C_{get} = \varepsilon_0 \varepsilon_r W/L \), where \( \varepsilon_0 = 8.85 \times 10^{-12} \) F/m is the permittivity of free space, \( \varepsilon_r = 3.9 \) is the relative permittivity of SiO2, \( W \) and \( L \) are the width and length of the nanostructure channel in the device, and \( t = 1 \) \( \mu \)m is the thickness of the dielectric (SiO2).

Using \( g_m = -26 \) nS at \( V_d = 1 \) MV, the room temperature hole mobility was estimated to be \( 346 \) cm2/V·s and the hole concentration was estimated to be \( 2.78 \times 10^{18} \) cm\(^{-3}\). The mobility and concentration values were fairly consistent over additional devices. The measurements carried out on two additional devices produced \( (\mu_h, n_h) \approx (346 \text{ cm}^2/\text{V s}, 2.27 \times 10^{18} \text{ cm}^{-3}) \) and \( (316 \text{ cm}^2/\text{V s}, 1.98 \times 10^{18} \text{ cm}^{-3}) \). These additional Te devices were fabricated from several weeks old Te nanostructures which were stored in a nominally N2 purged atmosphere.
box after synthesis. It is important to note that we did not observe significant changes in electrical properties between freshly synthesized and several weeks old Te nanostructures. The predicted hole mobility for multiple layers of α-Te is on the order of $10^3$–$10^4$ cm$^2$/V s in an ideal scattering condition, i.e., scattering is contributed only by acoustic phonons. However, the measured hole mobility is likely to be affected by impurities, charge traps, and contacts, resulting in a smaller value of hole mobility.

The highest room temperature hole mobility reported for 2D-like Te nanostructures is $\sim$700 cm$^2$/V s for a 16 nm thick Te nanostructure, which is higher than the obtained hole mobility in this experiment. Nevertheless, the obtained hole mobility is higher than or similar to other reported experiments on Te nanostructures as shown in Table I, as well as that of other van der Waals materials such as MoS$_2$ which exhibits a typical mobility of $\sim$190 cm$^2$/V s. Additionally, electrical resistivity is inversely proportional to the product of mobility and carrier concentration. Therefore, the electrical resistivity in these Te nanostructures is lower than the previous reports as summarized in Table I. The performance of our Te device and the hole mobility is comparable to black phosphorous on the Si/SiO$_2$ substrate which exhibits a typical mobility of $\sim$400 cm$^2$/V s.

In summary, we have demonstrated the high temperature synthesis of ultrathin pure Te nanostructures by vapor phase deposition using ZrTe$_2$ powder as a source material. Nanowirelike Te nanostructures were obtained with thicknesses down to $\sim$3 nm.
TABLE I. Summary of electrical properties of Te from this work and literature.

| Reference                  | Mobility (cm²/V s) | Density (cm⁻³) | Thickness (nm) | Comments       |
|---------------------------|--------------------|----------------|----------------|----------------|
| This work                 | ~350               | 1.8 x 10¹⁸     | 20             | Nanowire       |
| 3                         | 700                | 1 x 10¹⁸       | 16             | ZnO             |
| 13                        | ~250²              | 2 x 10¹⁸       | 12             | ZnO             |
| 1                         | 700, 420³          | 3.8 x 10¹⁸     | 40             | Film           |
| 10                        | 163                | 7.8 x 10¹⁸     | 55             | Film           |
| 27                        | 299                | 1.28 x 10¹⁸    | 40             | Film           |
| 32                        | 250                | 1–3 x 10¹⁸     | 40             | Film           |
| 1                         | 41                 | 2 x 10¹⁸       | 55             | Film           |
| 33                        | 10                 | 2 x 10¹⁸       | 55             | Film           |
| 25                        | ~250               | ~5 x 10¹⁷      | bulk           |                |

Table 1: Summary of electrical properties of Te from this work and literature.

*Mobility at Vₓ = 0 V.
²Device fabricated on the growth substrate (transfer-free).
³Nanostructures transferred to different substrates for device fabrication.

EDS study confirms that these nanostructures do not contain Zr down to the detection limit of the instrument. Room temperature electric properties were investigated by fabricating single nanostructure devices on SiO₂/Si substrates. These nanostructures exhibit superior room temperature electrical conductivity compared to bulk and nanostructures of Te previously synthesized by other, lower temperature wet chemical or physical vapor deposition methods. We also observed high room-temperature field effect hole mobility in these nanostructures comparable to black phosphorus when measured using similar device configurations. Based on these results, we conclude that high temperature vapor phase growth using ZrTe₃ as a source material can lead to superior quality Te nanostructures for future device applications.

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