Synthesis of Highly Anisotropic Semiconducting GaTe Nanomaterials and Emerging Properties Enabled by Epitaxy

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Pseudo-1D materials are a new class of materials where atoms are arranged in chain-like structures in 2D. Examples of these materials include recently discovered black phosphorus,[1,2] ReS$_3$, and ReSe$_2$ from transition metal dichalcogenides (TMDCs),[3–5] TiS$_3$, and ZrS$_3$ from transition metal trichalcogenides,[6–9] and most recently gallium telluride (GaTe).[10] The presence of structural anisotropy impacts their physical properties and leads to direction-dependent light–matter interactions,[11,12] dichroic optical responses,[8] high mobility channels,[2] and anisotropic thermal conduction,[3] which are especially attractive for optoelectronic and photonic applications.[13]

Despite numerous reports on the vapor phase growth of isotropic TMDCs and post-transition metal chalcogenides (PTMCs) such as MoS$_2$,[12] and GaSe,[13] the synthesis of pseudo-1D materials is particularly difficult due to the anisotropy in interfacial energy, which stabilizes dendritic growth rather than single crystalline growth with well-defined orientation.[5,14] The growth of monoclinic GaTe has been demonstrated on flexible mica substrates with superior photodetecting performance.[15] In this work, we demonstrate that pseudo-1D monoclinic GaTe layers can be synthesized on a variety of other substrates including GaAs (111), Si (111), and c-cut sapphire by physical vapor transport (PVT) techniques. High-resolution transmission electron microscopy (HRTEM) measurements, together with angle-resolved micro-photoluminescence (ARMP) and angle-resolved micro-Raman (ARMR) techniques, provide for the very first time atomic scale resolution experiments on pseudo-1D structures in monoclinic GaTe and anisotropic properties. Interestingly, GaTe nanomaterials grown on sapphire exhibit highly efficient and narrow localized emissions, which are found to be related to select types of line and point defects as evidenced by photoluminescence (PL) and Raman mapping scans. Detailed spectroscopic studies reveal unique features of these sharp subband emissions, which distinguish themselves from the broad defect emissions normally found in semiconductors. It also makes the samples grown on sapphire more prominent than those grown on GaAs and Si, which demonstrates more regular properties. Overall findings offer new routes to synthesize pseudo-1D GaTe layers, provide synthesis insights and epitaxy relations, and establish their anisotropic optical performance. These unique properties open new opportunities for GaTe to find applications in novel optoelectronic devices that have been established in the PTMC family.[16]

Synthesis and Structural Characteristics: In this work, GaTe flakes were synthesized by the PVT technique in a tube furnace (Figure S1, Supporting Information) using GaTe and Ga$_2$Te$_3$ polycrystalline powders as the source. A detailed description of the growth process can be found in the Experimental Section. We have performed the growth on a variety of substrates including GaAs (111), Si (111), and c-cut sapphire to understand different substrate effects and the growth mechanism. Here, GaAs and Si wafers were selected in order to integrate 2D material systems into scalable bulk semiconductors in hybrid structures, and sapphire was chosen owing to recent successful growth of 2D systems onto their highly crystalline surfaces.

As shown in Figure 1a,b, the morphology of the GaTe nanostructures depends strongly on the substrate type. Typical growth processes carried onto GaAs and Si yield GaTe nanowires lying flat on the surface; however, some of the ribbons also grow out of plane at an acute angle with the substrate, as shown in scanning electron microscopy (SEM) images in Figure 1a,b. These nanowires appear to be well aligned along three directions that make a fixed angle of 120° with each other, which is a sign of epitaxial growth.[17] To confirm the epitaxial relationship between GaTe and GaAs, we performed pole figure X-ray diffraction (XRD), SEM, and HRTEM. A full XRD spectrum of the sample is shown in Figure S2 (Supporting Information). GaAs (111) and (222) peaks are clearly seen, confirming the (111) orientation of the GaAs substrate. As for GaTe, only two peaks are revealed—the (001) peak at 11.9° and the (002) peak at 23.8°. This suggests that the GaTe nanowires have a (002) preferred orientation on GaAs(111) as shown in Figure 1d. The pole figure XRD result shown in Figure 1c further confirms that the GaTe (002) plane is parallel to the GaAs (111) plane (Figure 1d and the inset of Figure 1e).

Next, we determine the rotational relationship between the GaTe nanowires and the GaAs substrate by analyzing the angle of the nanowire growth. Figure 1e shows the SEM image of the GaTe nanowires grown at the edge of the GaAs wafer.
It is known that the GaAs (111) wafer cracks along the [110] direction. We find that the nanowires form a 30° angle with respect to the wafer edge, which is parallel to the [121] direction of GaAs (Figure 1f). The HRTEM image (Figure S3, Supporting Information) shows that the nanowire growth direction is along the [010] chain direction of GaTe. Thus the rotational relationship between GaTe and GaAs is determined as GaTe [010]//GaAs [121]. It is worth noting that the growth of GaTe is quite different in that instead of isotropic growth (i.e., material grows in all directions in the plane), monoclinic GaTe growth occurs preferably along the [010] chain direction. This chain-like growth is directly related to the highly anisotropic crystal structure of monoclinic GaTe and will be discussed later in this Communication. Here, we also note that similar relations also exist for GaTe grown onto Si wafers but are not shown here for brevity. However, due to the large lattice mismatch of 13.7% between GaTe (4.15 Å of Te–Te distance along [010]) and sapphire (4.81 Å along [010]) compared to 2.0 and 7.2% on GaAs (d_{GaAs} = 4.07 Å along [110]) and Si (d_{Si,Si} = 3.87 Å along [110]), respectively, GaTe flakes grow rather randomly on sapphire substrates as shown in Figure 2a. The resulting morphology varies from wires to flakes with the dimensions ranging from 10 to 30 µm. This random distribution of morphology and dimension may be attributed to the van der Waals epitaxy growth mechanism where the GaTe is bonded to the substrate by weak van der Waals force without forming any direct chemical bonds. Under this regime, the GaTe atoms can transport more freely on the sapphire surface. Overall, our manufacturing route enables synthesis of pseudo-1D GaTe sheets for the first time onto different substrates and is a significant progress in the synthesis of pseudo-1D systems.

Optical Response of PVT-Deposited GaTe: To understand how substrate type and growth characteristics influence the overall optical response from the direct band gap nanomaterial GaTe, we have performed PL measurements as shown in Figure 2b. We find that the GaTe flakes grown on sapphire behave quite differently from those grown on GaAs and Si, as well as flakes isolated from GaTe single crystals synthesized via the Bridgman method. The main PL peak located at 1.66 eV for GaTe/sapphire (red) and GaTe/GaAs (green) matches closely the fundamental
direct band gap of GaTe at 1.65 eV (blue line), and is thus identified as the band edge emission ($X_0$) related to radiative recombination of photoexcited electrons and holes. The sample grown on GaAs displays an additional peak at 1.39 and 1.66 eV for the two flakes. Surprisingly, however, the sample grown on sapphire (red line) shows three additional sharp (FWHM $\approx$ 50 meV) emission lines at 1.29, 1.39, and 1.50 eV as pointed out by the blue arrows which are not present in exfoliated GaTe and GaAs/GaTe samples. Then the question arises: What is the origin of these additional peaks?

As evidenced by micro-Raman measurements, we safely exclude the presence of secondary phases such as Ga$_2$Te$_3$ or TeO$_2$ and their potential impact on the PL spectrum. As shown in Figure 2c, Raman spectra from sapphire/GaTe precisely match the GaTe single crystals grown by the Bridgman method, GaAs/GaTe, as well as existing literature without any additional peaks associated with other compositions and phases. The Raman measurements were performed on various spots and none of them showed the possible existence of a second phase. Other direct evidence for single phase GaTe comes from our selected area electron diffraction (SAED) patterns and energy dispersive X-ray spectroscopy (EDS) mapping in large areas on a GaTe flake synthesized on sapphire (Figure S4, Supporting Information). In agreement with our earlier Raman data, the
SAED shows the flake is pure crystalline GaTe without any second phases. The EDS mapping also indicates a uniform distribution of Ga and Te elements. However, the SAED does suggest that the flake is poly-crystalline and is composed of two domains with different crystal orientations, which will be discussed later with the anisotropy properties. The HRTEM image (Figure 3b) also proves the high crystallinity of the GaTe flake.

To elucidate the origin of these new PL peaks, we performed large area spatial mapping of the PL spectra on two typical flakes grown on sapphire under 488 nm laser excitation with particular focus on the two most prominent PL peaks, namely, 1.39 eV (X\text{sub}) and 1.66 eV (X\text{0}). However, similar conclusions can also be drawn for other below band gap emission peaks in Figure 2b. Overall, PL mapping data show that emission peak position and intensity are relatively nonuniform across the flake as shown in Figure 2e. The X\text{0} emission is observed all across the flake for both flakes 1 and 2, and is particularly strong at certain boundaries and edges. The X\text{sub} emission line, however, is only observed at selected boundaries and edges, as shown in Figure 2e,f, suggesting spatially localized emission. A line scan of the PL spectra across flake 2 can be found in Figure S5 (Supporting Information), which clearly demonstrates that the X\text{sub} emission is only localized at the edges.

Temperature-dependent PL measurements (100–300 K) in Figure 2g show that FWHM of X\text{0} and X\text{sub} both remain fairly sharp at all temperatures (15 and 22 meV, respectively). Below 150 K an additional, broad (FWHM ~123 meV) peak appears at 1.55 eV. This peak is also seen at 4 K as shown in Figure S6 (Supporting Information). In contrast to X\text{sub}, this broad peak, which thermally quenches above 100 K, can be attributed to randomly arranged defects with shallow confinement, such as Ga vacancies that have been studied recently.[19] High signal-to-noise photoreflectance spectra at 4 K (Figure 2h) show that the sharp differential reflectance (dR/R) peak (blue dashed line) matches closely in energy with the X\text{0} PL emission line (orange solid); i.e., we do not observe any Stokes shift due to localization of Coulomb bound electron–hole pairs (excitons) at this energy. This clearly demonstrates that the emission comes from radiative recombination of excitons at the direct band gap around 1.78 eV.[20] Here, we note that the blueshift of the X\text{0} emission from 1.66 eV at room temperature to 1.78 eV at low temperature is simply due to an increase in optical band gap, which can be described by the Varshni law;[21] the exciton binding energy of around 20 meV (bulk GaTe) is only a small correction.[20] Similarly, X\text{sub} peak position shifts from 1.39 eV at 300 K to 1.5 eV at 4 K, but the photoreflectance spectrum does not display any transition peak at 1.5 eV. The absence of the reflectance transition proves that the X\text{sub} has a comparably low density of states and oscillator strength, and is not related to any strong band-to-band transition. We argue that X\text{sub} originates from recombination of electron–hole pairs at localized energy levels at 1.39 eV (localized emission centers). This can be clearly seen in our power-dependent PL studies: As shown in Figure 2i the X\text{sub}/X\text{0} peak intensity ratio quickly decreases and the X\text{sub} peak saturates as the laser power density is increased. This behavior is another indication for a low density of states.
and suggests recombination of carriers spatially localized at defects to be the origin of $X_{\text{sub}}$.

Using different laser excitation energies, we provide further evidence that shows that $X_{\text{sub}}$ does not come from the band-to-band transition of a second phase but structural defects in GaTe. Figure 2j shows the PL spectra at excitation energies above the band gap (1.96 eV), resonant with the band gap (1.771 eV) and below the band gap (1.621 and 1.6 eV). Carriers excited resonantly at the band gap can clearly relax very efficiently toward $X_{\text{sub}}$, which suggests that defects can capture a considerable fraction of the generated excitons. As expected from this scenario, we observe that laser excitation below the gap results in much lower defect related $X_{\text{sub}}$ emission as the absorption (i.e., exciton generation) is strongly diminished.

The significance of this $X_{\text{sub}}$ emission can be described as follows: (i) This emission is clearly seen at low temperature (4 K) and room temperature, suggesting either strong confinement at defect sites or the formation of a mid-gap defect band. This looks similar to the intermediate band emission found in ZnTe$_{1-x}$Se$_x$ recently, which indicates the possibility of below band gap absorption and intermediate band solar cells based on GaTe; (ii) The emission is spectrally very sharp with an FWHM similar to the band edge emission $X_0$, which is abnormal for a defect emission. Both observations (i) and (ii) are in clear contrast to $X_{\text{sub}}$, which only appears at low temperature and is spectrally broad. Further studies have been planned for determining what kind of defects give rise to $X_{\text{sub}}$ exactly. One possibility is O$_2$ adsorption as it has been recently, which indicates sub exactly. One possibility is O$_2$ adsorption as it has been widely used in other pseudo 1D materials such as ReS$_2$ and TiS$_3$. The measurement is carried out in the same setup as the ARMP experiment. Figure 3d shows the angle-resolved Raman intensity of two $A_g$ modes (116 and 212 cm$^{-1}$) and one $B_g$ mode (164 cm$^{-1}$). The anisotropy of the two $A_g$ modes shows a twofold symmetry with a period of 180°. The 116 cm$^{-1}$ mode exhibits maximum intensities along the (010) chain direction, while the 212 cm$^{-1}$ mode is polarized perpendicular to the chain direction. The opposite polarization behavior indicates different atomic displacement directions for the two modes. On the other hand, the polarization of the 164 cm$^{-1}$ mode shows a fourfold symmetry with a 90° period, and the intensity reaches maximum at 45°, 135°, 225°, and 315°, making a 45° with respect to the (010) chain direction. The different polarization features for the $A_g$ and $B_g$ modes are consistent with recent reports on GaTe anisotropy and can be explained by different symmetries of the $A_g$ and $B_g$ vibration modes.

As shown in Figure S4 (Supporting Information), the GaTe flake consists of two domains with different crystal orientation and a grain boundary in between. The SAED pattern shows that each domain is single crystalline with the (010) chains parallel to the edge. Note that the flake in Figure S4 (Supporting Information) is half the shape of a bowtie-shaped GaTe flake as shown in Figure 3c, which is probably due to damage caused by sonication when preparing the sample. As a result, the whole flake can be divided into four domains indicated by the rectangles in Figure 3c. To further understand the domain structure of the bowtie-shaped GaTe flake, we have performed ARMP measurements in different domains on the bowtie-shaped flake as shown in Figure S7 (Supporting Information). The result shows that the 116 cm$^{-1}$ mode is always polarized along the edge direction, which is the (010) chain direction and agrees with the SAED result. The polarization of the 164 and 212 cm$^{-1}$ modes is also consistent with the crystal orientation in each domain. Thus domains 1 and 3 have the same orientation, whereas domains 2 and 4 have the same orientation. The ARMP result further confirms that the crystal orientation is along the (010) chain direction at the edge of the bowtie-shaped GaTe flake, which is consistent with recent work on an exfoliated material.

Present work establishes the synthesis of anisotropic, direct gap, and semiconducting monoclinic GaTe on various substrates including GaAs (111), Si (111), and c-cut sapphire for the first time. Interestingly, nanomaterials grown on sapphire exhibit well-defined, narrow, and bright PL emission peaks originating from localized emission due to a select type of
imperfection site states that appear at energies well below the fundamental emission line (optical band gap). Bright emission within the forbidden band is observed for the first time in GaTe and may be the starting point for further defect engineering for optoelectronics in PTMCs. Lastly, angle-resolved PL and Raman studies suggest that the synthesized monolinic GaTe flakes are also highly anisotropic due to their unique crystal structure, which is the first demonstration of the anisotropy in vapor phase synthesized pseudo 1D GaTe.

Experimental Section

Sample Preparation: The PVT synthesis of GaTe flakes was carried out in a tube furnace with a 1” quartz tube. GaTe (60 mg) and Ga2Te3 (10 mg) powders (American Elements) were mixed together as the source materials, and Ar (15 sccm)+H2 (5 sccm) was used as the carrier gas. GaAs (111), Si (111), and c-cut sapphire wafers were used as growth substrates. Prior to growth the GaAs substrates were cleaned by piranha solution followed by dilute hydrogen chloride (HCl) solution. Si wafers were cleaned with acetone, methanol, RCA-1 cleaner (mixture of deionized (DI) water, 27% NH4H2O, and 30% H2O2 with volume ratio 5:1:1), and 2% hydrogen fluoride (HF) solution. C-cut sapphire wafers were cleaned by oxygen plasma for 5 min. The source powders were loaded in a quartz boat and sent to the center of the tube. The substrate was located 10 cm away from the center. The tube was evacuated out in a tube furnace with a 1” quartz tube. GaTe (60 mg) and Ga2Te3 source materials, and Ar (15 sccm) were used as growth substrates. GaTe powders were preheated to 650 °C for 5 min and then cooled down to room temperature. The Ar flow rate was set at 15 sccm and the growth pressure was 30 Torr for the whole process. The GaTe bulk crystals were synthesized by the modified Bridgman growth technique[4] in a single zone furnace at temperatures ranging from 850 to 1020 °C for three weeks.

Materials Characterization: Room temperature PL and Raman measurements for the GaTe flakes were performed in a Renishaw InVia spectroscopy system with a 100x objective lens using a laser source of 488 nm wavelength. The laser was focused onto the sample with a spot diameter of 0.5 μm. Angle-resolved measurements were carried out in the same system by mounting samples on a rotation stage and taking data when the sample was rotated every 20°. The incident laser and detector were polarized parallel to each other along the 0–180° direction. Low-temperature PL and reflectance measurements were performed in a home built microspectroscopy setup built around a closed cycle, low vibration attoDry cryostat with a temperature controller (T = 4–300 K). For PL at a fixed wavelength of 633 nm an He-Ne laser was used; for PL experiments as a function of excitation wavelength we used a tunable, continuous wave Ti-Sa Laser SOLSTIS from M SQUARED. The PL experiments as a function of excitation laser wavelength we used a halogen lamp with a stabilized white light source for reflectivity. Vibrational measurements were performed in a Renishaw InVia spectrometer and detected by an Si-CCD camera. The morphology of the sample was studied by scanning electron microscopy using a Hitachi S4700 field-emission SEM with a working distance of 12–15 mm and an acceleration voltage of 15–20 kV. TEM samples were prepared by dispersing the GaTe flakes in isopropyl alcohol (IPA) through sonication and dropping the IPA onto copper grids with holey carbon films.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.


