1D Germanium Sulfide Van Der Waals Bicrystals by Vapor-Liquid-Solid Growth

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Abstract

Defects in two-dimensional and layered materials have attracted interest for realizing properties different from those of perfect crystals. Even stronger links between defect formation, fast growth, and emerging functionality can be found in nanostructures of van der Waals crystals but only a few prevalent morphologies and defect-controlled synthesis processes have been identified. Here, we show that in vapor-liquid-solid growth of 1D van der Waals nanostructures, the catalyst controls the selection of the predominant (fast-growing) morphologies. Growth of layered GeS over Bi catalysts leads to two coexisting nanostructure types: Chiral nanowires carrying axial screw dislocations and bicrystal nanoribbons where a central twin plane facilitates rapid growth. While Au catalysts produce exclusively dislocated nanowires, their modification with an additive triggers a switch to twinned bicrystal ribbons. Nanoscale spectroscopy shows that, while supporting fast growth, the twin defects in the distinctive layered bicrystals are electronically benign and free of nonradiative recombination centers.

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INTRODUCTION

Defects play a central role in crystal growth. In the absence of defects, growth of single crystals requires costly homogeneous nucleation on the perfect facets. Continued growth can become essentially barrier-free in the presence of self-perpetuating steps on the growth surface, which are usually associated with screw dislocations.¹⁻² Alternatively, in absence of screw dislocations, other defects can provide sites for heterogeneous layer nucleation where the activation energy can be significantly reduced so as to support rapid growth. Twins and twinned interfaces, for example, can reduce the nucleation barrier by providing preferential nucleation sites at the re-entrant twin groove.³ Hence, the presence of screw dislocations or twins facilitates fast crystal growth. In vapor-liquid-solid (VLS) growth of nanowires of 3D-crystalline materials, either screw dislocation⁴⁻⁶ or twin driven⁷ growth mechanisms have been observed. While the VLS growth of Ge, Si, and GaAs nanowires usually yields wires oriented along the [111] crystallographic direction irrespective of the orientation of the underlying substrate,⁸⁻¹² the twin plane re-entrant mechanism has been reported to lead to formation of nanowires with different crystal orientations⁷ in a variety of materials, including GaAs,¹³⁻¹⁴ ZnO,¹⁵ Si,¹⁶⁻¹⁸ SiGe,¹⁹ and InAs.²⁰ Twins can also induce morphologies such as nanosails in InSb.²¹

Defects in planar 2D and layered crystals have been studied extensively as they can promote different functionalities and defect engineering routes.²²⁻²⁶ Nanostructures of van der Waals crystals show even stronger links between defect formation, accelerated crystal growth, and defect-induced functionality. A prototypical example are van der Waals nanowires. Synthesized by Au-catalyzed VLS growth,²⁷ germanium sulfide (GeS) nanowires form as growth spirals around an axial screw dislocation that ensures rapid,

barrier-free growth while introducing a chiral (helical) structure and, *via* Eshelby twist,²⁸ a tunable interlayer twist²⁹⁻³⁰ that makes such nanowires attractive for twistronics.³¹ Here we show that synthesis of 1D nanostructures of one and the same van der Waals crystal can involve different defect-mediated growth modes, spiral growth around axial screw dislocations and twin plane re-entrant growth, and we demonstrate that it is possible to switch between different defect fast-growing morphologies by modifying the VLS catalyst. We find that Bi as a low-melting single-component VLS catalyst simultaneously yields chiral twisted van der Waals nanowires with axial screw dislocations and ultrathin bicrystal nanoribbons with a characteristic central twin plane. While Au-catalyzed VLS growth consistently yields chiral twisted nanowires,²⁹ modifying the Au catalyst by introducing small amounts of SnS vapor along with the primary GeS precursor switches the growth to the formation of bicrystal van der Waals ribbons, analogous to those obtained over Bi catalysts, along with a small number of other fast-growing nanoribbon morphologies.³²⁻³³ Transmission electron microscopy (TEM) and electron diffraction establish the morphology, structure and stacking of the 1D bicrystals observed here. Cathodoluminescence spectroscopy on individual bicrystal ribbons demonstrates that, while enabling fast growth rates, the central twin defect is electronically benign, *i.e.*, does not introduce gap states acting as nonradiative recombination centers.

RESULTS AND DISCUSSION

1D GeS nanostructures were prepared in a tube furnace reactor by evaporation of GeS powder onto Si(100) substrates covered by a thin Bi film (see Methods for details). At substrate temperatures of 300°C, we find the formation of dense forests of GeS nanostructures on the Bi covered Si substrate (Fig. 1a, b). Scanning electron microscopy

(SEM) images show that all nanostructures have high-aspect ratio and similar length, but adopt two different morphologies: (i) straight single-crystalline GeS nanowires; and (ii) nanostructures with distinctly different shape – flat and wide at the base and tapering down to a uniform width closer to the tip. The morphology of these two families of 1D structures was investigated using TEM and HAADF-STEM. Fig. 1c shows that the straight nanostructures are chiral twisted GeS nanowires carrying axial screw dislocations (Fig. S1).



Figure 1. 1D GeS nanostructures synthesized by VLS growth on Bi catalysts. a. Scanning electron microscopy (SEM) of high-yield Bi-catalyzed GeS nanostructures on the Si(100) growth substrate. **b.** Higher magnification SEM image showing the flat, fin-like tapered base and uniformly narrow tip region of the synthesized nanostructures. **c.** TEM image of a straight chiral twisted GeS nanowire obtained by VLS growth over Bi catalyst, carrying the usual axial screw dislocation (sd). Scale bar: 100 nm. **d.** HAADF-STEM image of one of the concurrently grown GeS nanostructures near the transition from the tapered base to the narrow tip-region with nearly uniform width. **e.** HAADF-STEM image of the same nanostructure close to the tip. Scale bars in d., e.: 1 µm. Arrows in d. and e. mark the same position along the nanostructure. **f.** Higher magnification TEM image of the same GeS nanostructure in the vicinity of the Bi catalyst particle at the tip, showing a distinct, sharp boundary along the centerline, identified below as a twin boundary (tb). Scale bar: 100 nm.

The distinct second nanostructure type with wide base is shown in Fig. 1d-f. It consists of

a characteristic saw-tooth like lateral expansion in size towards the base (Fig. 1d, lower

half), while maintaining a nearly uniform width over lengths of several tens of μ m toward its tip (Fig. 1e). Higher-magnification TEM clearly shows the Bi VLS catalyst particle at the tip (Fig. 1f). Close to the tip this particular nanostructure appears very straight and uniform with a width of ~38 nm, and it shows a characteristic sharp boundary along its centerline that runs along the entire length and divides the nanostructure into two equal parts.

Nanobeam electron diffraction (Fig. 2a-d, Fig. S2-S3) demonstrates that the two halves are single crystalline GeS, viewed along the [010] zone axis. The electron diffraction patterns from the two crystalline halves are identical but they are oriented differently, showing mirror symmetry with respect to the boundary in the center. Thus, we conclude that the second type of GeS nanostructure obtained by VLS growth with Bi catalyst is a 1D bicrystal containing a single longitudinal twin boundary at its center. Nanometerresolved electron diffraction across the bicrystals (Fig. S2) and high-resolution TEM (Fig 2d; see also Fig. S4) demonstrate that the longitudinal twin boundary is sharp and the two parts of the bicrystal highly symmetric. In both halves, the van der Waals stacking is along the *c*-axis ([001] direction) as in layered bulk GeS, while the bicrystal symmetry axis is parallel to the [104] direction. High-resolution TEM confirms that the (001) planes on both sides have mirror symmetry (Fig. 2d). Statistical analysis of TEM data shows angles between (001) planes across the twin boundary of 60° and ~112° (Fig. 2f). Observed widths range from over 100 nm to below 18 nm.

Electron diffraction patterns of the catalyst particles at the tip confirm single-crystalline rhombohedral Bi (Fig. 2e).³⁴ In all investigated GeS bicrystals seen along the [010] zone axis, the Bi particle shows a fixed orientation ([$\overline{101}$] zone axis, Fig. 2, Fig. S3), *i.e.*, the bicrystal growth front templates its oriented crystallization upon cooling. The Bi particle

invariably appears asymmetric with respect to the twin boundary. In Bi-catalyzed GeS nanowires (Fig. 1c, S1), the crystallized Bi catalyst particles are oriented relative to the



Figure 2. 1D GeS bicrystals synthesized on Bi/Si(100) substrates. a. TEM image of a GeS bicrystal close to the Bi VLS catalyst at the tip. **b. - c.** Nanobeam electron diffraction patterns of the single crystalline GeS regions on both sides of the twin boundary. **d.** High resolution TEM image of the longitudinal twin boundary at the center of the bicrystal. **e.** Nanobeam electron diffraction pattern of the Bi tip. **f.** Histogram showing the distribution of the angles between the (001) planes on either side of the twin boundary. **g.** Schematic of the morphology of the GeS bicrystals.

GeS basal planes so that $\{110\}^{Bi} \parallel \{001\}^{GeS}$. Similarly, in the GeS bicrystals we find that the $\{110\}^{Bi}$ planes align with one set of $\{001\}^{GeS}$ basal planes. However, given the typical angles between GeS (001) planes across the twin boundary (Fig. 2f), this relationship can be fulfilled only for one half of the bicrystal (Fig. S3-S4). Nanobeam diffraction patterns taken with a step of 1 nm across the GeS-Bi interface on both sides of the longitudinal twin boundary (Fig. S3) confirm that one of the bicrystal halves shows the $\{110\}^{Bi} \parallel \{001\}^{GeS}$ orientation relationship, in this case the bottom crystal (Fig. S3fh).

Bi-catalyzed GeS nanowires have van der Waals layers stacked along the nanowire axis, and harbor ubiquitous axial screw dislocations that are instrumental to the growth of the wires and are responsible for their chiral structure (Fig. S1).^{29,35} In Bi-catalyzed GeS bicrystals we find the presence of another defect, a longitudinal twin boundary, which can also support fast growth. Steady-state growth driven by a single twin at the center of a nanowire has been demonstrated for 3D-crystalline (Ge) nanowires,⁷ where nucleation of new atomic layers at the growth front occurs at the groove of the twin boundary and proceeds to complete consecutive (111) planes, preventing each of the sides of the twin from growing faster and outgrowing the other. In Bi-catalyzed van der Waals bicrystals, the growth front is formed by GeS (001) planes (usually enclosing angles of 60°, see Fig. 2f) that appear to have grown simultaneously as they are symmetric over the entire length of the bicrystals. During VLS growth the Bi catalyst is liquid and hence expected to wet the two halves of the bicrystal symmetrically, stably positioned in the V-groove at the growth front. If the two half-crystals are bonded at the interface, a single nucleation event at the twin plane (akin to twin plane re-entrant growth, but here realized for a van der Waals crystal) will be sufficient to add new GeS layers on either side of the boundary. The asymmetric positioning of the Bi particle observed at room temperature follows from the cooling and crystallization of the catalyst. Since the two GeS half-crystals are symmetric, identical in size, and are both terminated by (001) facets, the crystallizing Bi catalyst selects an orientation in which the GeS (001) basal facet on one side of the twin boundary lies parallel to its (110) planes.

To show that the VLS catalyst controls the formation of bicrystals, we demonstrate the switching between chiral twisted GeS nanowires and of GeS bicrystals by modification of a Au VLS catalyst. In prior work, we obtained different GeS nanoribbon geometries by evaporation of GeS and SnS powders at low ratio between SnS and GeS vapor pressures

(p(SnS):p(GeS) ~0.04) and substrate temperatures between 265-300°C.³² VLS growth using a pure Au catalyst invariably results in the synthesis of GeS nanowires with axial screw dislocations as a fast-growing defect morphology. Small amounts of co-evaporated SnS act as a growth modifier without being significantly incorporated (see Methods for details), and leads to the formation of GeS bicrystals at all substrate temperatures between 265-300°C, along with tilted ribbon-like 1D GeS nanostructures reported previously.³² Growth at lower temperatures generally produces thinner bicrystals. Use of modified Au catalysts therefore opens the temperature window for obtaining bicrystals compared to growth with Bi catalysts, where these structures are found only at 300°C. TEM images of representative GeS bicrystals grown over modified Au catalysts are shown in Fig. 3. The bicrystals are easily recognized by the characteristic twin plane at

their center. Structurally they are identical to the Bi-catalyzed GeS bicrystals (direct comparison is provided in Fig. S5 and Fig. S6). The morphology is also very similar. Measured angles between the (001) planes are again mostly ~60°, with a small minority showing obtuse angles near 110° (Fig. 3f). Bicrystals with obtuse angles grown over modified Au catalysts tend to taper near the tip and carry small catalyst particles (Fig. 3 (b)), and a similar taper is also observed for the minority population of Bi-catalyzed bicrystals with larger angles between mirrored (001) planes (see Fig. 2a). In contrast, the majority of nanostructures with 60° twinning angles has constant width over most of the length (Fig. S7). Electron diffraction obtained in plan-view geometry again shows [010] zone axis GeS patterns for both halves (Fig. 3d, e) whose (001) planes on either side are symmetrically tilted with respect to the bicrystal axis.

A main difference in the bicrystal morphologies with the two types of catalysts is seen near the base of the nanostructures. Bi-catalyzed bicrystals show wide, fin-like bases (Fig. 1) whereas bicrystals grown over modified Au catalysts appear straight (i.e., without significant taper) down to the substrate. To explore these differences, and in particular the modifications from GeS VLS growth over a pure Au catalyst (resulting in nanowires with axial screw dislocations) to VLS growth over Bi and SnS-modified Au catalysts (giving rise to bicrystals with axial twin defects), we obtained SEM images at the early growth stage (Fig. S8). Since we have never observed a switching between different defect morphologies within individual nanostructures, we conclude that the catalyst-induced selection between dislocated nanowires and twinned bicrystals likely involves a different configuration of the VLS catalyst on the substrate during the initial exposure to precursor vapor. This assumption is supported by the observations shown in Fig. S8. Dewetted Au catalyst particles exposed to the GeS vapor under our growth conditions show mostly compact (circular) footprints (Fig. S8a), consistent with the subsequent VLS growth of GeS nanowires. Modification of the Au catalyst by adding SnS causes strongly elongated nuclei (Fig. S8b) that template the formation of bicrystal nanoribbons. Bi has shown a tendency of forming elongated islands on Si substrates.³⁶ SEM images suggest that these elongated Bi islands template an initially wide bicrystal that gradually narrows and ultimately terminates in a tip region with constant width (Fig. S8c). While these results suggest that the catalyst-substrate interaction plays a key role in selecting between dislocated nanowires and twinned bicrystal ribbons, differences between the twinned morphologies with modified Au and Bi catalysts may originate from other effects, such

as catalyst wetting on the growing ribbons or non-specific incorporation of GeS vapor into the ribbon edges.



Figure 3. Morphology of GeS bicrystals grown over modified Au catalysts. a. HAADF-STEM image of a characteristic segment of a GeS bicrystal grown from GeS vapor with traces of SnS vapor on dewetted Au on Si (100). b. Higher magnification STEM image close to the tip, showing the small remnant of the Au catalyst. c. STEM image of a fragment of a GeS bicrystal showing a characteristic 60° angle between mirrored (001) crystal planes on either side of the twin boundary. d, e. Nanobeam electron diffraction recorded on the two sides of the twin boundary of the bicrystal shown in c. f. Histogram showing the distribution of angles between the GeS (001) basal planes (the preferred fracture planes) on either side of the twin boundary. g. Schematic of the flat bicrystal with GeS layers seen along the *b*-direction ([010]), mirrored at the twin boundary (tb).

Cathodoluminescence in scanning transmission electron microscopy (STEM-CL) was used to investigate the optoelectronic properties of individual GeS bicrystals, particularly to detect a possible quenching of the luminescence due to non-radiative recombination processes at the planar defect. Panchromatic CL maps show electron stimulated light emission from the entire bicrystals, with highest intensity observed for excitation near the



Figure 4. Nanometer-scale electron beam excited light emission from individual GeS bicrystals. a. HAADF-STEM image of a GeS bicrystal. **b.** Panchromatic STEM-CL map. **c.** Hyperspectral CL linescan across the bicrystal (between arrows in (a)). **d.** Comparison of individual CL spectra obtained at the center and near the edge of the bicrystal (positions marked by colored arrows in c). Dark gray symbols show a CL spectrum obtained from a thick, bulk-like GeS flake at 300 K, while light gray symbols correspond to luminescence of the bulk GeS flake at 110 K.³⁷ **e, f.** Comparison of CL spectra obtained in the center and at the edge of the bicrystal, respectively. Gray circles: Measured spectra. Shaded regions: Gaussian lineshape analysis. Solid black lines: Overall fits to the data. Gaussian components of the same color in panels (e) and (f) are centered at the same photon energy. BE: Main band edge luminescence peak (see also Fig. S10).

edges (Fig. 4a, b). A hyperspectral CL linescan across the bicrystal (Fig. 4c) shows strong light emission with characteristic intensity distribution from the edges and the center of the bicrystal. Electron beam excitation at the edges yields intense and broad light emission (Fig. 4d). Spectra excited at the center of the bicrystal show a dominant peak at \sim 1.9 eV photon energy (Fig. 4d). Fitting the spectra generally requires multiple Gaussian components, centered below as well as above the fundamental bandgap. Spectra obtained in the center and at the edge can be fitted by sets of Gaussian components centered at the same peak energies, albeit with different intensities due to the different emission geometry, *i.e.*, extended planar surface near the center *versus* abrupt termination of the crystal at the edge. At the center of the bicrystal, the spectral composition is the same as

for bulk GeS,³⁸ consisting of an intense band-edge luminescence peak and a shoulder to lower photon energies (Fig. 4e). The main difference is that the band-edge emission in the bicrystals is strongly blue-shifted (~ 0.3 eV) from the bulk bandgap of GeS (~1.62 eV, see Fig. 4d; Fig. S10),³⁷⁻³⁸ consistent with quantum confinement in the GeS van der Waals bicrystals (see Fig. S10).²⁹ Intralayer confinement in bicrystals is caused by the small thickness of the ribbons, which translates into a small lateral size of the individual GeS van der Waals layers along the *b*-direction ([010], Fig. S10). Comparing with reported confinement shifts in CL of single GeS nanowires,³⁵ we find that the 0.3 eV blue shift observed in Fig. 4d corresponds to a thickness of ~70 nm, in good quantitative agreement with the actual thickness of that ribbon (67 nm) determined from the beamcurrent attenuation in STEM,³² confirming that the blue-shifted emission of our bicrystal ribbons is indeed due to confinement effects (Fig. S11). Defect related luminescence components in the bandgap, on the other hand, show smaller blue shifts. These



Figure 5. Nanometer-scale electron beam excited light emission from two different GeS bicrystals. a. HAADF-STEM image of a GeS bicrystal with characteristic GeS light emission. b. Panchromatic STEM-CL map. c. CL spectrum at the center of the bicrystal (dashed line in b). d. HAADF-STEM image of a GeS bicrystal with anomalous light emission. e. Panchromatic STEM-CL map, showing quenched luminescence along the centerline between 1.85 – 2.0 eV (arrow). f. CL spectrum at the center of the bicrystal (dashed line in (e)). Note the complete absence of the band-edge peak (BE) that dominates most bicrystal CL spectra as shown in c. and Fig. 4.

conclusions are supported by a direct comparison of multi-Gaussian lineshape analyses for GeS bicrystal ribbons and bulk GeS flakes, shown in Fig. S10 and discussed in the Supporting Information. Shorter bicrystal segments, finally, show interference of propagating waveguide modes reflected by the specular end facets (with a progressive blue shift of the band-edge peak due to a change in thickness and confinement; Fig. S9), similar to GeS flakes.³⁷

Measurements on several GeS bicrystals confirm the same characteristic CL spectra with bulk-like emission at the center, unaffected by the presence of the twin boundary (Fig. 5a – c). Occasionally, however, we observe anomalous light emission from GeS bicrystals grown on Au-catalysts modified by small amounts of added SnS vapor (Fig. 5d – f). Most



Figure 6. Electron beam-current dependent CL spectroscopy. a. HAADF-STEM image, **b.** Panchromatic STEM-CL map of a thicker (~215 nm, Fig. S11) GeS bicrystal nanoribbon suitable for electron beam-current dependent CL spectroscopy. **c.** STEM-CL spectra of the bicrystal ribbon shown in panels a and b, for different exciting beam currents (measured at T = 138 K). **d.** Fits of equation (1) to beam-current dependent CL spectra obtained at three different temperatures. **e.** Spontaneous emission quantum efficiency, η , determined from the fit parameters A_{CL} , B_{CL} , and C_{CL} (obtained from the fits shown in d) using equation (2).

of the fit components of the anomalous spectra closely match those of typical spectra except for a quenching of the band-edge luminescence, which is completely suppressed (Fig. 5e, f). The quenching of band-to-band radiative recombination typically indicates the appearance of a non-radiative (Shockley-Read-Hall, SRH)³⁹⁻⁴⁰ recombination channel with short carrier lifetime, associated with mid-gap states. In conventional semiconductors, such trap states are often associated with transition metal impurities (*e.g.*, Cu, Fe, Au in Si).⁴¹ The predominance of 'clean' GeS spectra with intense band-edge peaks indicates that the twin boundary is electronically benign, *i.e.*, does not suppress radiative recombination.

To further support this conclusion, we carried out STEM-CL spectroscopy with different exciting electron-beam currents (Fig. 6). Analogous to pump-power dependent photoluminescence,⁴² the exciting beam current (I_{CL}) is expressed as powers of the CL signal (L_{CL}) with coefficients for different recombination processes denoted as A_{CL} , B_{CL} , and C_{CL} , for SRH, radiative, and Auger recombination, respectively:

$$I_{CL} = A_{CL} (L_{CL})^{1/2} + B_{CL} L_{CL} + C_{CL} (L_{CL})^{3/2}$$
(1)

The coefficients A_{CL} , B_{CL} , and C_{CL} are determined by fitting equation (1) to experimental beam current-CL intensity (I_{CL} - L_{CL}) relationships, measured on a thicker GeS bicrystal ribbon suitable for this analysis (Fig. 6a, b) at three temperatures (Fig. 6c, d), from which the spontaneous emission quantum efficiency, η , can be estimated as:

$$\eta = \left[1 + \frac{A_{CL}}{B_{CL}} (1 - \gamma_r) (L_{CL})^{-1/2} + \frac{C_{CL}}{B_{CL}} (1 - \gamma_r) (L_{CL})^{1/2}\right]^{-1}$$
(2)

where γ_r denotes the fraction of the spontaneous emission that is reabsorbed by the active region. The results of this analysis are shown in Fig. 6e, adopting the most conservative choice of the photon recycling factor, $\gamma_r = 0$. The measurements demonstrate that GeS

bicrystal ribbons are excellent optoelectronic nanostructures, with CL intensities that are nearly independent of temperature as well as unity or near-unity spontaneous emission quantum efficiencies at low temperatures (T = 138 K) and at room temperature, respectively. Heating above room temperature leads to a reduction in quantum efficiency and a shift of the peak in η towards lower beam current (*i.e.*, CL intensity), consistent with a non-zero C_{CL} parameter due to the onset of Auger recombination.

The electronically benign nature of the twin boundary is consistent with results of density functional theory calculations (Fig. S12), which surveyed some of the possible relaxed twin boundary configurations and obtained their corresponding formation energy and density of states (DOS). With the exception of the highest-energy structure where a significant density of gap states are introduced both at the edge and at the twin boundary, all surveyed structures showed minimal changes in the DOS (added states near the conduction band edge) between defect-free bulk GeS and sites at the edges or near the twin boundary in the interior. There are two possible metal species present in the VLS catalyst, Au and Sn, which could give rise to trap states in bicrystals with anomalous CL spectra. Calculations show minimal energy cost of substituting Ge by Sn, both in the interior and at the twin boundary, *i.e.*, incorporation of Sn appears feasible. TEM shows strain contrast at the twin boundary in some of the bicrystals grown with SnS-modified Au catalysts (Fig. S6) that is not observed in Bi-catalyzed bicrystals grown from pure GeS vapor. Even though both Sn and Au are below the detection limit in energydispersive X-ray spectroscopy (EDS), the observed strain suggests the possible decoration of the boundary with one of these impurities.

CONCLUSIONS

Our results support the growing recognition that specific defect structures with reduced activation energies for layer nucleation - or avoiding the need for nucleation altogether produce the fastest growing and therefore dominant types of 1D nanostructures of 2D van der Waals crystals. In particular, we demonstrated that in the vapor-liquid-solid growth of 1D van der Waals nanostructures the catalyst controls the selection of the predominant, fast-growing morphology. Growth of GeS, an anisotropic layered semiconductor, over Au VLS catalysts yields exclusively chiral twisted nanowires, *i.e.*, growth spirals with axial screw dislocations in which a perpetuated edge at the growth front enables incorporation of the precursor without the need for nucleation of new layers. Replacing the Au catalyst by Bi leads to two coexisting nanostructure types: Dislocated nanowires and bicrystal nanoribbons, in which a central twin plane facilitates rapid growth. The same twinned bicrystals are also accessible by modifying a Au catalyst with an additive, here small amounts of SnS evaporated together with the main GeS growth precursor. The bicrystals, all of which are of high crystal quality, show predominant 60° twin boundaries as well as occasional obtuse angles near 110° between the stacked van der Waals layers on either side of the twin. Observations at the early growth stages show that a conversion from compact circular shapes of Au catalysts to elongated shapes of the supported Bi and SnS-modified Au catalysts correlates with the switch from growth of dislocated GeS nanowires to twinned bicrystal ribbons.

Nanoscale spectroscopy shows that, while supporting fast growth, the twin defects in the layered GeS bicrystals are electronically benign and free of nonradiative recombination centers. As a result, estimated spontaneous emission quantum efficiencies are near unity

16

from low temperatures all the way to room temperature. This is true for bicrystals synthesized over modified Au catalysts where possible Au incorporation at the twin defect might be expected to induce deep level trap states. As a result, the GeS ribbons show luminescence characteristics similar to bulk GeS flakes, albeit with strongly blueshifted band-edge emission due to intralayer carrier confinement as a result of the limited size of the individual GeS sheets stacked in the ribbons.

As an important difference to the previously reported chiral twisted GeS nanowires synthesized by VLS growth over Au and Bi catalysts,^{27,29-30,35} the GeS bicrystal nanoribbons reported here grow in a much more forgiving process. While Au- and Bi-catalyzed twisted GeS nanowires can be realized only in a narrow temperature window centered at 300°C (\pm 5°C), use of a SnS-modified Au catalyst opens up the temperature window for synthesis of twinned GeS nanoribbons, which are obtained down to at least 245°C. Hence, the GeS bicrystal ribbons represent nanostructures with excellent optoelectronic properties that can be produced *via* a robust VLS growth process.

More broadly, the reported results demonstrate that twin-plane re-entrant growth, previously established for 3D crystalline materials and nanostructures, can become the dominant growth mechanism for nanostructures of van der Waals crystals if a suitable catalyst is used to direct the growth process into this defect morphology. While we showed efficient, confinement-tunable light emission for the GeS bicrystals realized here, translating the catalyst-induced morphology switching to other van der Waals materials, *e.g.*, those from which nanowires have already been obtained by VLS growth, will open a wide range of additional functionalities including those of semiconductors for electronics

and optoelectronics (*e.g.*, for van der Waals crystals such as SnSe,⁴³ In_2Se_3 ,⁴⁴ or Sb_2Se_3 ⁴⁵), topological insulators (Bi₂Se₃, Bi₂Te₃),⁴⁶ *etc*.

METHODS

GeS nanostructure growth with Bi catalyst: GeS powder (99.99%; Sigma Aldrich) was heated to 450°C in a pumped quartz tube reactor with two temperature zones, while the substrate consisting of Si(100) covered with a Bi film (2-3 nm thick, deposited by magnetron sputtering) was heated to growth temperatures of 300°C for a growth duration of 5 minutes. During growth, a carrier gas flow (Ar, 99.9999%; Matheson) was maintained at 60 standard cubic centimeters per minute (sccm) and a pressure of 20 mTorr.

GeS nanostructure growth with SnS-modified Au catalyst: GeS powder (99.99%, Sigma Aldrich) and SnS powder (99.99%, Sigma Aldrich) precursors were placed in separate quartz crucibles and heated to 450° C (~480 mTorr vapor pressure) and 650° C (~50 mTorr vapor pressure), respectively, in the same quartz tube reactor but using a separate quartz liner to avoid cross-contamination. The zone containing the substrates (Si(100) wafers covered with Au films (2-4 nm thick, deposited by magnetron sputtering) was typically heated to a growth temperature of 275° C; high-quality GeS bicrystal nanoribbons were obtained at substrate temperatures between 245 - 300°C. During growth, a Ar-2% H₂ carrier gas flow (99.9999%; Matheson) was maintained at 60 sccm and a pressure of 20 mTorr. Growth was typically performed for 10 minutes, resulting in the formation of nanostructures with lengths of several tens of micrometers.

SEM and TEM imaging: In both cases nanostructure forests on the native growth

substrate were imaged using scanning electron microscopy in a FEI Helios Nanolab 660 field-emission microscope at 5 keV primary beam energy. Structure and morphology of individual nanostructures were investigated by (scanning) transmission electron microscopy ((S)TEM) in an FEI Talos F200X equipped. For the TEM experiments, several thousand bicrystals were spread on carbon supports.

Cathodoluminescence in STEM: The optoelectronic properties of individual bicrystals were investigated by cathodoluminescence spectroscopy performed in STEM mode (STEM-CL) using a Gatan Vulcan CL holder at room temperature, 200 kV electron energy, and incident beam currents of 300-600 pA. Panchromatic CL maps (512×512 pixels, 1.28 ms per pixel) were acquired by scanning the exciting electron beam across the bicrystals and recording the emitted light intensity across a broad wavelength range (400-1000 nm). Hyperspectral linescans were acquired by displacing the electron beam in predefined equal steps across individual nanostructures and acquiring full CL spectra (integration time: 10 s per spectrum) at each beam position. Individual CL spectra shown in the figures were extracted from such linescan datasets.

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Supporting Information: Supporting Figures S1-S11: Additional TEM imaging and electron diffraction on Bi- and Au-catalyzed bicrystal GeS nanoribbons; SEM imaging at early growth stages; cathodoluminescence spectroscopy of a short GeS bicrystal segment; comparison of CL spectra of GeS bicrystals and bulk flakes; density functional theory calculations of energies of different twin boundary structures and associated density of states. Comparison of GeS bicrystal and bulk GeS CL spectra. Computational Methods. Supporting References.

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