Highly Anisotropic Mechanical and Optical Properties of 2D Layered \( \text{As}_2\text{S}_3 \) Membranes

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Supporting Information

ABSTRACT: Two-dimensional (2D) materials with strong in-plane anisotropy are of interest for enabling orientation-dependent, frequency-tunable, optomechanical devices. However, black phosphorus (bP), the 2D material with the largest anisotropy to date, is unstable as it degrades in air. In this work we show that \( \text{As}_2\text{S}_3 \) is an interesting alternative, with a similar anisotropy to bP, while at the same time having a much higher chemical stability. We probe the mechanical and optical anisotropy in \( \text{As}_2\text{S}_3 \) by three distinct angular-resolved experimental methods: Raman spectroscopy, atomic force microscopy (AFM), and resonance frequency analysis. Using a dedicated angle-resolved AFM force deflection method, an in-plane anisotropy factor of $E_a / E_c = 1.7$ is found in the Young’s modulus of \( \text{As}_2\text{S}_3 \) with $E_{a\text{-axis}} = 79.1 \pm 10.1 \text{ GPa}$ and $E_{c\text{-axis}} = 47.2 \pm 7.9 \text{ GPa}$. The high mechanical anisotropy is also shown to cause up to 65% difference in the resonance frequency, depending on crystal orientation and aspect ratio of membranes.

KEYWORDS: mechanical anisotropy, 2D materials, arsenic trisulfide (\( \text{As}_2\text{S}_3 \)), Raman spectroscopy, multimode resonances, nanoelectromechanical systems (NEMS)

After the first exfoliation and characterization of graphene in 2004,1 2D crystals have attracted much interest as suspended membranes in mechanical systems due to their unprecedented high elastic moduli and strength.2−5 Although resonators of many 2D materials, such as graphene and MoS\(_2\), have been widely studied,5−8 there are only a few 2D crystals known that exhibit large in-plane anisotropy.9−14 Black phosphorus (bP) shows the largest known anisotropy in Young’s modulus among 2D materials15,16 with a ratio of $E_a / E_c = 2$ along the in-plane axes ($b$ and $a$). However, few-layer bP is stable in air for only several minutes,17 which severely affects its mechanical properties after oxidation18 and complicates its application and integration into complex nanoelectromechanical systems (NEMS).

Here, we discuss the exfoliation of \( \text{As}_2\text{S}_3 \) including in its monolayer form and the fabrication of suspended membranes of this material. Although \( \text{As}_2\text{S}_3 \) has been studied and applied in its bulk and amorphous form, it has not received much attention in its ultrathin exfoliated form. The anisotropy in the Raman spectrum of \( \text{As}_2\text{S}_3 \) is compared to the mechanical anisotropy in its static deflection probed by atomic force microscopy (AFM) and in its dynamic deflection probed by a change in the resonance frequency of mechanical modes. We show that thin layers of \( \text{As}_2\text{S}_3 \) have a mechanical anisotropy comparable to that of black phosphorus, while their stability against degradation in ambient air facilitates integration and...
study of few-layer As$_2$S$_3$ resonators in complex mechanical devices. In addition to that, the material has perspectives to become an important member of the class of 2D materials due to a unique combination of properties: As$_2$S$_3$ is known to transmit infrared well, has an optical indirect band gap of $\sim 2.6$ eV, shows photoconductivity, and has a large acousto-optical figure of merit. This combination of properties makes it of interest for fundamental studies of anisotropic phenomena in 2D materials, but can also enable new types of applications such as acousto-optic modulators.

RESULTS AND DISCUSSION

Structure and Characterization. Arsenic trisulfide, also known as orpiment, is a naturally occurring layered crystal. The unit cell of the As$_2$S$_3$ lattice consists of two layers inverted by a symmetry center located in a van der Waals gap (Figure 1b). From the crystallographical point of view, a unit cell of arsenic trisulfide can be well exfoliated, as indicated by the tapping mode AFM measurements in Figure 1d, which show an exfoliation energy comparable to graphite. These properties make it of interest for fundamental studies of anisotropic phenomena in 2D materials, but can also enable new types of applications such as acousto-optic modulators.

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Figure 2. (a) Raman spectra of a bulk As2S3 crystal (thickness, $t \approx 50$ nm) for a polarization of incident red laser light ($\lambda = 632$ nm) along two crystalline axes ($a$ and $c$). (b) Polarization-dependent Raman intensity spectra obtained by sample rotation with normal incident light (along the $b$-axis of a crystal). (c) Thickness-dependent Raman spectra under $\lambda = 632$ nm excitation. (d–f) Polarization dependence for three Raman-active modes. Vibrational modes in a, b, and d–f are labeled in accordance to previous works on As$_2$S$_3$.

Figure 3. Detailed angle-resolved study of the Young’s modulus of As$_2$S$_3$. (a) Tapping mode AFM image of the sample. Scale bar: 4 $\mu$m. (b) Typical force–deflection curve obtained at different angles of a rectangular cavity with respect to crystalline axes. Top inset: Optical image of the sample. Scale bar: 8 $\mu$m. Bottom inset: Principle of the measurement. (c) Angle-resolved effective Young’s modulus of the membrane. Red line is a fit to $\text{eq } 2$. Young’s moduli for in-plane crystalline directions ($E_a$ and $E_c$) are indicated. (d) Raman spectra along each axis. (e) Effective Young’s modulus along $a$ and $c$ crystalline axes measured for the best five samples of various thickness (from 9 to 25 nm).
powers. Although As$_2$S$_3$ is known to transmit infrared well$^{19}$ approaching the band gap of the material ($\sim$2.6 eV$^{21,46}$) with excessive light can convert the crystal to its amorphous state,$^{47}$ thus locally destroying the crystallinity of the flake (see SI 1). Taking this into account, we further used flakes of thicknesses $t > 8$ nm and a corresponding low power of the incident laser light to minimize damage to the suspended As$_2$S$_3$ membranes.

**Anisotropy in the Static Mechanical Properties.** The strong asymmetry of the crystalline structure of As$_2$S$_3$ along the $a$- and $c$-axes (Figure 1b,c) is also expected to cause a large anisotropy in the Young’s modulus of the material.$^{48}$ We have studied the mechanical anisotropy in the Young’s modulus as a function of angle by AFM using the star-shaped configuration shown in Figure 3a. With an AFM tip of calibrated stiffness we indent the As$_2$S$_3$ membranes suspended over star-shaped trenches and record the force–deflection curve at the center of each of the 12 membranes of the same flake. The high aspect ratio of the rectangular membranes, $b > a$ is chosen such that the slope of the force–deflection curve is dominated by the effective Young’s modulus, $E_{\text{eff}}$, along the shortest side of the rectangle. As shown in Figure 3b, a difference in deflection, $\delta$, was achieved for an equal force applied, $F$. Assuming a point force deflection at the center of the cavity, we obtain the following equation for the force–distance relation of the rectangular membrane (see SI 4):

$$F = \frac{E_{\text{eff}} t^3}{12 a (1 - \nu^2) a^2} \delta + C_2 N_\theta \delta + \frac{c_0}{(1 - \nu^2) a^2} E_{\text{eff}} t^3$$

(1)

where $a(a, b)$, $C_2(a, b)$, and $c_0(a, b)$ are geometry-dependent factors and $N_\theta$ is the intrinsic pretension. Using Poisson’s ratio $\nu^2 = 0.094$,$^{49,50}$ we fit eq 1 to the data and extract effective Young’s moduli along the angles to the crystalline axes. We take into account measured thickness variations as determined by AFM, which are found to be at most one to two single layers (as seen in Figure 3a), to extract correct values of $E_{\text{eff}}$. Figure 3c shows the characteristic dumbbell shape of angle-resolved effective Young’s moduli, which is a typical example of mechanical anisotropy in layered materials.$^{16}$ We also measure Raman spectra along the hard and soft axis of the crystal to connect the observed anisotropy in mechanical properties to the crystalline orientation (Figure 3d). The dependence of $E_{\text{eff}}$ on the rotation angle, $\theta$, in a particular direction is defined from Hooke’s law, taking into the account $E_{\text{eff}}$, $E_a$, and an effective shear, $G_{\text{eff}}$ (see SI 5):$^{16}$

$$E_{\text{eff}}(\theta) = \frac{1}{\frac{E_a}{\cos^4 \theta} + \left(\frac{1}{G_{\text{eff}}} - \frac{1}{E_a}\right) \sin^2 \theta \cos^2 \theta + \frac{1}{E_a} \sin^4 \theta}$$

(2)

From the fits of eq 2 to the data in Figure 3c,e we obtain $E_a = 79.1 \pm 10.1$ GPa, $E_i = 47.2 \pm 7.9$ GPa, and $G_{\text{eff}} = 28.0 \pm 2.5$ GPa, so that the ratio of the mechanical anisotropy is $E_a/E_i \approx 1.7$ (Figure 3e). These values are also consistent with additional measurements done on synthetically grown As$_2$S$_3$ showing that effect of possible defects and stacking faults on mechanical anisotropy in natural As$_2$S$_3$ crystals is insignificant (see SI 6).

**Dynamic Mechanical Properties.** When As$_2$S$_3$ is suspended over a rectangular hole made in a Si/SiO$_2$ substrate, it forms a resonator. We use the light intensity modulation by the motion of the membrane to measure the resonance frequencies in a laser interferometer. A schematic of the setup is shown in Figure 4a. Here, the modulated blue diode laser is used to optothermally drive the As$_2$S$_3$ membrane and the red laser to read out its motion.$^{51}$ This allowed us to observe a significant shift in the resonance frequency of the fundamental mode, $f_0(\theta)$, at $\theta = 90^\circ$ to the hard axis ($a$-axis) of the crystal (Figure 4b). We were also able to resolve the natural mode frequency as a function of crystalline orientation of a membrane and compare it to the effective Young’s modulus extracted for the same flake with the force–deflection AFM measurements. As shown in Figure 4c, the ratio of anisotropy measures $\frac{E_a}{E_i} = \left(\frac{f_0(\theta)}{f_0(90)}\right)^2 = 2.0 \pm 0.3$ in the dynamic experi-
ment, which is comparable to $\frac{E_b}{E_a} = 1.8 \pm 0.1$ found from the static deflection of the same flake. This confirms the significant effect of anisotropy in the Young’s modulus on the mechanical response of the membranes.

We further investigated the evolution of higher modes of thick rectangular As$_2$S$_3$ resonators as a function of the angle to the crystalline axis. We transferred a 129 $\pm$ 3 nm thick flake, as measured by tapping mode AFM, over a set of rectangular cavities with a $b:a = 2:1$ side ratio (Figure 5b). This aspect ratio results in mode crossings at certain angles, $\theta$, and a more complex frequency dependence on angle for higher modes. In Figure 5a,c the solid lines show the results of a finite element method (FEM) model obtained using the COMSOL Multiphysics package of the first six modes of a clamped As$_2$S$_3$ plate resonator. The model matches experimental data well (Figure 5a and c) for the first four modes. Note that no fitting parameters were used, with only the thickness measured from AFM and elastic constants of As$_2$S$_3$ added as an input to the FEM simulations. For higher modes we observe a discrepancy between the measured position of the resonance peak and the model, which could be due to a larger sensitivity of higher modes to perturbations and imperfections of the system. $^{51}$ We show six modes obtained from FEM simulation together with five experimentally detected modes in Figure 5c to emphasize that the highest measured mode could not be precisely identified but is likely to be related to either the fifth or sixth mode of the resonator. Interestingly, as can be seen in Figure 5a, an avoided crossing is expected when the long side of the rectangular membrane with $b/a = 2$ aspect ratio makes an angle of 40° with respect to the $c$-axis of the crystal. This unique feature could be potentially used in further studies of strong intrinsic coupling and internal resonances between modes in rectangular resonators of different ratio of sides. $^{52}$

CONCLUSIONS

In conclusion, we combined optical and mechanical characterization techniques to obtain a comprehensive picture of the in-plane anisotropy in arsenic trisulfide. Using polarization-dependent Raman spectroscopy and force–deflection AFM in a star-shaped geometry of rectangular cavities, we systematically characterized the mechanical anisotropy in a few layers of this van der Waals crystal and relate that to its crystalline structure and orientation. We showed quantitatively that the anisotropy in the Young’s modulus of As$_2$S$_3$ is close to that of black phosphorus, which is currently known to have the largest in-plane $\frac{E_b}{E_a}$ ratio among 2D crystals. $^{15}$ We also demonstrated that this results in a large orientation-specific change in the resonance frequency of higher vibrational modes in As$_2$S$_3$ resonators. These mechanical properties make As$_2$S$_3$ an interesting alternative to black phosphorus for applications in flexible strain-dependent optoelectronic devices, while stability in air makes it a promising material for further integration into optomechanical nanodevices as well as for research of anisotropic nonlinear mechanics in the 2D limit. We also believe that, due to its high flexibility and pronounced optoelectronic properties, $^{79,66}$ As$_2$S$_3$ has perspectives to find applications in atomically thin optical waveplates and to become an interesting candidate material for polarization-sensitive flexible photoconductors $^{12,24}$ and acousto-optic modulators. $^{24}$

METHODS

Sample Fabrication. A prepattern on a Si/SiO$_2$ (285 nm) chip was implemented by reactive ion etching (RIE), and edges were examined to be well-defined by scanning electron microscopy (SEM) and AFM. Flakes of As$_2$S$_3$ were exfoliated from a matrix crystal mined in Senduch, Sakha Republic, Russia. Thin flakes of As$_2$S$_3$ were transferred on a prepatterned chip by an all-dry viscoelastic stamping method. $^{39}$

Raman Spectroscopy. Raman spectroscopy studies were performed on a Horiba Scientific LabRAM HR at an excitation of $\lambda_{\text{exc}} = 632$ nm, $\lambda_{\text{mon}} = 514$ nm, and $\lambda_{\text{sam}} = 488$ nm in a backscattering geometry in parallel-polarized configuration, ($c_p \parallel c_s$) with a 360° rotational sample stage. All measurements were performed away from the suspended region.

Atomic Force Microscopy. AFM scans and inspections were performed in tapping mode on a Bruker Dimension FastScan AFM. Cantilevers were chosen to have a tip radius of $\sim$7–10 nm, as confirmed by SEM imaging. Using thermal and solid surface deflection calibration we estimated the spring constant, $k$, for each cantilever. We use cantilevers with spring constants of $k = 30–40$ N/m for thicker flake ($>$12 nm) and $k = 8–9$ N/m for thinner ones ($<12$ nm). Each data point on the polar diagram in Figure 3a is an averaged value from fitting three to five force–deflection curves obtained at the same position.

DOI: 10.1021/acsnano.9b06161
ACS Nano 2019, 13, 10845–10851

Figure 5. Change in resonance frequency of vibrational modes of an As$_2$S$_3$ plate. (a) Finite element model (FEM) for the first six modes of a resonator compared to the measured magnitude ($M_a$, $M_b$) of resonance peaks at 0° and 90° rotation of the rectangular membrane with respect to the $c$-axis of the crystal. (b) Optical image of a device with orientation and scales indicated. Dimensions are $a = 5$ $\mu$m and $b = 10$ $\mu$m. Scale bar: 5 $\mu$m. Both blue and red lasers are focused at the position indicated by the red circle in the lower panel. (c) Vibrational mode frequencies with corresponding errors compared to the FEM model.
Laser Interferometry. The sample is mounted on a motorized xy nanopositioning stage inside a vacuum chamber with optical access. A modulated diode laser (λ = 405 nm) was used to excite the membrane optothermally and drive it into motion. An interferometric displacement detection is then obtained by focusing a He–Ne laser beam (λ = 632 nm) on the suspended membrane while recording the interfering reflections from the membrane and the Si substrate underneath using a photodiode. Laser spot size is on the order of ~1 μm. The photodiode signal is processed by a vector network analyzer. The pressure inside the vacuum chamber is kept stable at ~1 × 10⁻⁶ mbar.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsnano.9b06161.

ACKNOWLEDGMENTS

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