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ABSTRACT

The development of photonic integrated circuits would benefit from a wider selection of materials that can strongly control near-infrared (NIR) light. Transition metal dichalcogenides (TMDs) have been explored extensively for visible spectrum optoelectronics; the NIR properties of these layered materials have been less-studied. The measurement of optical constants is the foremost step to qualify TMDs for use in NIR photonics. Here, we measure the complex optical constants for select sulfide TMDs (bulk crystals of MoS2, TiS2, and ZrS2) via spectroscopic ellipsometry in the visible-to-NIR range. We find that the presence of native oxide layers (measured by transmission electron microscopy) significantly modifies the observed optical constants and need to be modeled to extract actual optical constants. We support our measurements with density functional theory calculations and further predict large refractive index contrast between different phases. We further propose that TMDs could find use as photonic phase-change materials, by designing alloys that are thermodynamically adjacent to phase boundaries between competing crystal structures, to realize martensitic (i.e., displacive, order–order) switching.

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Integrated photonics offers a way to create all-optical circuits to reduce the power needed to move and process massive data flows and to move beyond-von Neumann computing.1,2 Essential for photonic circuits are active materials that can modulate the phase and amplitude of light to perform switching, logic, and signal processing; if these changes are nonvolatile, then they can also be used for memory. The interaction length required to produce a substantial modulation of the optical phase is \( L \sim \lambda_0 / \Delta n \), where \( \lambda_0 \) is the free-space wavelength and \( \Delta n \) is the refractive index change. For instance, well established photonic material LiNbO3 produces a refractive index change of order 0.001 at typical supply voltages for electro-optic modulation and therefore requires a large interaction length \( L > 1 \) mm. A leading class of active materials that can strongly modulate near-infrared (NIR) light on a sub-micrometer length scale are the so-called phase-change chalcogenides, such as those found in the Ge-Sb-Te (GST) system.3 These materials operate by switching between crystalline and amorphous phases, which produce refractive index changes \( \Delta n > 1 \), but suffer from high optical losses in the NIR and sub-gigahertz phase-change operation.4–6 There is a need to expand the selection of materials available for phase-change functionality in the NIR for integrated photonics.

Transition metal dichalcogenides (TMDs) are layered materials (van der Waals-bonded solids) with intriguing physical properties that include layer-number-dependent bandgap, electron pseudospin, exciton and trion excitations, chemical tunability, catalytic action, polymorphism and phase-change behavior, and strong above-bandgap light absorption.7–11 The NIR and below-bandgap optical properties of TMDs have been little-studied.16–18 TMDs interact strongly with light and are expected to feature low-loss for below-bandgap wavelengths.
Polymorphism suggests that transitions between structural phases, such as the trigonal prismatic 2H and octahedral 1T (or distorted 1T’ and 1T’’), may be useful for optical switching.26,27 Transitions between 2H and 1T can be described by a simple translation of a plane of chalcogen atoms (a martensitic transformation).32 The layered, van der Waals crystal structure suggests that martensitic transformation strain may be low, which is beneficial for switching energy and fatigue. Phase-change functionality (i.e., transformation between layered polyphases) may be low, which is beneficial for switching energy and fatigue. Phase-change functionality (i.e., transformation between layered polymorphs) at room-temperature has been demonstrated for tellurides including MoTe2 and (Mo, W)Te2.21,23–25

In this manuscript, we focus on sulfide TMDs, because they have the largest bandgap (relative to selenides and tellurides) and therefore offer the largest spectral range for low-loss, below-bandgap operation. Unfortunately, the energetic cost of switching between phases is also highest for pure sulfides (relative to selenides and tellurides).33,34 We propose that alloying sulfide TMDs with different equilibrium structural phases, such as 2H MoS2 and 1T TiS2, could enable low-power switching. Specifically, these alloyed materials can be designed to be adjacent to a thermodynamic phase boundary.

Here, we measure the complex relative permittivity (ε = ε1 − iε2) of 2H-MoS2, 1T-ZrS2, and 1T-TiS2 bulk crystals in the visible-to-NIR region (300–2100 nm), using spectroscopic ellipsometry (SE). We find that in the NIR cannot be simply extracted by extrapolating from visible-light measurements and requires explicit measurements. We find that spectroscopic measurements must account for the presence of native oxide to avoid overestimating NIR loss. We support our measurements with density functional theory (DFT) calculations, which further predict a large refractive index contrast between 2H and 1T phases. We then suggest a paradigm to use TMD alloys as active phase-change materials for integrated photonics and use DFT to calculate alloy stability. Ellipsometry is a nondestructive optical technique that is widely used to measure the optical constants of thin films and bulk crystals.35,36 The technique involves measuring the ellipsometric ratio (ρ) of the amplitude reflection Fresnel coefficients for P- and S-polarized light (rP and rS, respectively) incident on a smooth surface. ρ is written as

\[ \rho = \frac{r_P}{r_S} = \tan(\psi) \exp(i\Delta), \]  

where ψ and Δ are the ellipsometric angles. ρ is a complex number and can be used to directly calculate real and imaginary optical constants, without relying on Kramers–Kronig (KK) relations. Relying on KK-constrained data can result in erroneous results, due to the extension of KK integral into spectral regions where measurements were not performed. Previous measurements have partially-characterized 2H-MoS2 bulk crystals and thin films, with limited information in the NIR.29,30,31 Much less information is available for 1T-ZrS2 and 1T-TiS2.32

We use thick TMD crystals to directly measure the dielectric properties in the NIR, without relying on models or extrapolation from visible-light measurements. For sufficiently-thick crystals, the light is absorbed completely, and there are no reflections from the back surface that can mix polarizations and cause measurement errors. We perform measurements on the mirrorlike faces of the as-received crystals, without any surface processing steps; below, we discuss how we account for the inevitable native oxide layer. We use two different ellipsometry instruments (Semilab SE-2000, and J. A. Woollam UV-NIR Vase) to ensure repeatability (see the supplementary material for details).

The procedure for extracting ε from measurements of ρ is greatly simplified by using bulk crystal, as opposed to thin films. For a bulk, isotropic material, ε can be directly calculated as

\[ \epsilon = \sin^2(\Phi) * \left( 1 + \tan^2(\Phi) * \left( \frac{1 - \rho}{1 + \rho} \right)^2 \right), \]  

where ε = ε1 − iε2, and Φ is the angle of incidence (AOI) relative to the surface normal direction.37 For TiS2, the effective “permittivity” and corresponds to a model of a pristine material interface with air, without a native oxide or any other overlayer. The presence of a native oxide can produce substantial errors including an overestimation of optical loss, as discussed below and in the supplementary material.

We use the results of DFT electronic structure calculations to predict dielectric functions using the random phase approximation, as described in the previous work and in the supplementary material.35,36 Briefly, we use Vienna ab initio simulation package (VASP), version 5.4,37–40 We treat the core and valence electrons by the projector-augmented plane wave method and approximate the exchange-correlation interaction by the generalized gradient approximation functional, implemented in the Perdew-Burke-Ernzerhof form.31,42 The energy minimization and force convergence criteria are 10–7 eV and 10–3 eV/Å, respectively.

The presence of a native oxide layer affects the experimental results in the entire spectral range and particularly for regions where the optical loss of the TMD is expected to be small, such as below the bandgap of MoS2 and ZrS2. We directly measured the thickness and composition of the native oxide using cross-sectional transmission electron microscopy (TEM) (see the supplementary material). On MoS2, we find a rough surface, possibly including a native oxide, approximately 2 nm thick. On ZrS2, we find a native oxide layer nearly 20 nm thick; similarly thick native oxide layers have been observed on ZrSe2.43 On TiS2, we saw no native oxide, within the imaging resolution of our experiment (~1 nm). Adding these overlayers to the optical model used to analyze the ellipsometry data significantly affects the extracted permittivity of MoS2 and ZrS2 (see the supplementary material for modeling details).

In Fig. 1, we present the experimentally-measured and theoretically-calculated in-plane complex permittivities for MoS2, TiS2, and ZrS2. The experimental data in Fig. 1 indicate the actual permittivity, determined by analyzing the ellipsometry data taking into account the native oxide layers. Of particular relevance for NIR photonics, ε1 is large below the bandgap of MoS2 and ZrS2 (indirect Eg = 1.1 and 1.6 eV, respectively, indicated by solid gray lines); TiS2 is a semimetal, (bandgap < 0.5 eV).45,46,47 The DFT calculations match fairly well the experimental data, both in magnitude and in spectral position of individual features. The A, B, and C excitons of MoS2 are well-resolved.48 For TiS2, the experimentally-observed peaks match in energy but are substantially broader than those calculated by DFT and are qualitatively similar to previously-reported measurements of TiSe2, indicating similar physical origins of the optical transitions.49 In ZrS2, the strongest direct gap excitonic oscillators (2.5 and 2.9 eV) are observed in both experiment and theory, although the experimental
data do not show the lowest-lying indirect gap transition near $E_g$. The 2.5 and 2.9 eV transitions are sufficiently close in energy to create zero-crossing of $\epsilon_1$ near 3.2 eV, which is not seen in the DFT calculations. Further discussion of the various optical transitions can be found in the supplementary material. Cross-polarization components are explicitly measured through generalized ellipsometry and are found to be $\sim 0$ for TiS$_2$ and MoS$_2$ (see the supplementary material).

The complex refractive index ($n - ik$) is related to $\epsilon$ by

$$n = \text{real}(\sqrt{\epsilon}), \quad k = -\text{imaginary}(\sqrt{\epsilon}). \quad (3)$$

$k$ is related to the absorption coefficient ($a = 4\pi k/\lambda$). In Fig. 2, we plot experimentally-measured $n$ and $k$ in the NIR spectral region 0.6–1.5 eV (827–2067 nm). All three materials have large $n$, comparable to or larger than that of silicon ($n_{\text{silicon}} \approx 3.4$), which is appealing for guiding NIR light. MoS$_2$ and ZrS$_2$ are indirect-bandgap semiconductors and have low-loss in the NIR. TiS$_2$ is semimetallic and has higher loss.

The loss coefficients ($k$) determined by experiment and reported in Fig. 2 are conditional on the particular samples measured and on our optical modeling and should be considered upper-bounds for these materials. In Fig. 2, we indicate $k$ determined from the effective permittivity [Eq. (3)], assuming no native oxide (dashed lines) and the value determined by optical modeling including native oxide thickness determined by TEM (solid lines). Taking the native oxide into account results in a lower value of the determined loss. Another important variable is the presence of defects, which contribute to below-bandgap absorption and optical loss.

Our samples are bulk crystals (including a naturally-occurring specimen of MoS$_2$) and definitely contain defects, including sulfur vacancies that contribute to NIR absorption.

Measurements on synthetic MoS$_2$ monolayers have shown lower loss in the NIR.

Our theoretical calculations are performed using models of perfect, defect-free crystals and predict substantially lower loss compared to the data. In Fig. 1, we show the calculated refractive index difference ($\Delta n$) between the 2H and 1T phases of bulk MoS$_2$. We here show results for the 1T’ phase instead of 1T because, according to our DFT calculations, 1T’ has lower energy than 1T for monolayer MoS$_2$ and therefore 1T may spontaneously relax to 1T’ in the zero-temperature limit. Compared to the 1T phase, the 1T’ phase has lower in-plane symmetry due to Mo–Mo dimerization, leading to optical trirefringence. In Fig. 3, we have averaged the results for the principal in-plane axes for consistency with the experimental literature, in which there is little evidence for strong in-plane anisotropy at room-temperature (this could be due to ferroelastic domain microstructure, or a reduced order parameter at relatively high temperature). We find that $\Delta n$ is large, comparable to or larger than that realized by phase-change materials in the GST system.

We focus on the NIR optical properties of sulfide TMDs because they offer lower optical loss (in NIR) than their selenide and telluride cousins, which have smaller bandgap. Unfortunately, the energetic cost of switching between phases is also highest for pure sulfides.

 Alloying sulfide TMDs with different reference states could enable low-power switching. The thermodynamics of TMD alloys are not well-established, and no phase diagrams have been published for the MoS$_2$-TiS$_2$-ZrS$_2$ ternary system, or the subsidiary binary systems. Here, we use DFT calculations to evaluate the likelihood of making alloy binary nanowires near the 2H-1T phase boundary (see supplementary material for calculation details).

In Fig. 4, we show the calculated Gibbs free energy-composition curves for the MoS$_2$-TiS$_2$ and MoS$_2$-ZrS$_2$ systems at 300 K. The results are very similar at 1000 K (not shown here), although with an overall downward shift of $\sim 1 \text{ eV/f.u}$ (formula unit) relative to the data at 300 K. For both systems, the free energy curves for the 2H and 1T phases cross at an intermediate composition, which is suggestive of a phase boundary. For the MoS$_2$-TiS$_2$ system, the curves are concave-downward and lie above the convex hull, which for this system is a straight line connecting the pure phases. Therefore, MoS$_2$-TiS$_2$ alloys will have a tendency to phase-separate at equilibrium. For the MoS$_2$-ZrS$_2$ system, we predict a solid solution in the 2H structure for $\text{Mo}_x\text{Zr}_{1-x}\text{S}_2$, $x > 0.75$, and phase...
separation for more Zr-rich compositions. For both of these systems, the relatively small energy difference between the alloy curves and the convex hull (<1 eV/f.u.) suggests that alloys may be kinetically-stabilized near the 2H-1T phase boundary. The ZrS$_2$-TiS$_2$ system is likely to be stable as a solid solution in the 1T phase, for which we do not calculate a significant positive enthalpy of mixing and therefore do not expect to observe spinodal decomposition. Future work should consider metastability and the kinetics of phase separation in TMD alloy systems, and a particular focus on low-temperature processing of TMD alloy thin films.

We measure the complex optical constants of select sulfide TMDs in a spectral range from the visible to the NIR. The samples are single-crystals of 2H-MoS$_2$, 1T-ZrS$_2$, and 1T-TiS$_2$ and are chosen to represent prototypes of the 2H and 1T structure types. All materials have high index of refraction ($n > 3$) and MoS$_2$ and ZrS$_2$ feature low-loss in the NIR. We find that the presence of native oxides significantly changes the observed optical constants, and these oxide layers need to be characterized and modeled. Further, our DFT calculations predict a large refractive index and strong contrast in optical properties ($\Delta n \sim 1$) between the different structure (phase) types, suggesting a role for TMDs as phase-change materials for integrated photonics. Achieving this goal will require making materials that are thermodynamically-adjacent to a phase boundary. For sulfides, this will likely require making materials that are thermodynamically-adjacent to a phase boundary. For sulfides, this will likely require...
alloying. We use DFT to calculate free energy-composition curves for alloys of MoS₂, ZrS₂, and TiS₂. The alloy structural phases become energetically degenerate at intermediate compositions, at which martensitic switching may be possible, if the alloys are found to be metastable or kinetically-stable.

See the supplementary material for information on: Experimental setup; attributing peaks to different transitions; transmission electron microscopy (TEM) characterization of surface; energy dispersive X-ray spectroscopy (EDS) of MoS₂ and ZrS₂ top surfaces; oxide and roughness modeling; TiS₂ with and without focusing optics; Mueller matrix (MM) measurements; theoretical calculations (DFT) for out-of-plane relative permittivity; multiple angle of incidence (MAI) measurements; effective ε for a range of ε₁ and εᵣ; and for different angle of incidence (AOI); density function theory (DFT) calculations; phase diagram calculation; and comparison with previously published data for MoS₂.

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The authors declare no competing financial interest.

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