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Near-infrared photonic phase-change properties of transition metal ditellurides
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ABSTRACT

We use the (Mo,W)Te\textsubscript{2} system to explore the potential of transition metal dichalcogenides (TMDs) as phase-change materials for integrated photonics. We measure the complex optical constant of MoTe\textsubscript{2} in both the 2H and 1T’ phases by spectroscopic ellipsometry. We find that both phases have large refractive index, which is good for confined light-matter interaction volume. The change $\Delta n$ between phases is of $\sigma(1)$, which is large and comparable to established phase-change materials. However, both phases have large optical loss, which limits to figure of merit throughout the measured range. We further measure the NIR reflectivity of MoTe\textsubscript{2} and Mo\textsubscript{0.91}W\textsubscript{0.09}Te\textsubscript{2}, in both the 2H and 1T’ phases. The data show that the strong optical contrast between the 2H and 1T’ structures persists even as the thermodynamic barrier between them is reduced by alloying. This bodes well for alloy design of phase-change materials.

Keywords: photonics, phase-change materials, layered materials, transition metal dichalcogenides, ellipsometry, reflectivity

1. INTRODUCTION

Integrated photonic circuits offer the possibility to process massive data flows with faster speed and lower energy consumption than electronic circuits, and to construct beyond-von Neumann computing architectures including functions such as compute-in-memory and deep learning.\textsuperscript{1,2} To fulfill the requirement of aggressively miniaturized integration, photonic materials should have strong light-matter interaction and process compatibility with other materials. Active photonic materials that can modulate the phase and amplitude of light are essential to perform basic operations including analog signal processing, logic computation, and storage. Particularly for active materials, low fatigue and excellent durability are necessary for the longevity of high-frequency devices.

The most well-established active photonic materials interact weakly with near infrared (NIR) light, and thus require a large interaction volume.\textsuperscript{3} The interaction length required for optical phase modulation could be estimated by $\lambda/\Delta n$, where $\lambda$ is the free-space wavelength, and $\Delta n$ is the refractive index change realized in the active material. For instance, commercially-established materials such as LiNbO\textsubscript{3} using the Pockels effect, and Si using the plasma dispersion effect, produce $\Delta n$ in the order of 0.001, and thus require millimeter-scale interaction lengths.\textsuperscript{4}

In contrast, phase-change materials such as the widely-studied Ge-Sb-Te (GST) system feature refractive index changes $\Delta n > 1$ between crystalline and amorphous phases,\textsuperscript{5,6} and are therefore of interest as active materials for integrated photonics. In these materials, phase-change functionality is based on time-temperature processing to achieve melt-quench and recrystallization transformations. This operating principle leads to high power consumption and fatigue problems (\textit{e.g.} poor durability for more than a billion cycles\textsuperscript{7}). Also, the operation frequency is limited to sub-GHz due to the kinetics of recrystallization.\textsuperscript{7,8}

In view of the need for active materials for integrated photonics, and the challenges presented by established phase-change materials, continued discovery and development of active materials is important. In this contribution we explore transition metal dichalcogenides (TMDs) as candidates for phase-change photonic materials. TMDs are layered materials with physical properties including electron pseudospin, exciton and trion excitations, strong above-band gap light absorption, polymorphism, and phase-change behavior.\textsuperscript{9–17} Weak van der Waals bonds between layers suggests process compatibility and easy integration with various material platforms, with reduced concerns over matching crystal structures or thermal expansion coefficients. The wide
chemical and crystallographic variety of TMDs provides flexibility for optimizing materials and composites for particular uses, including phase-change applications. In Figure 1 we illustrate four of the crystal structures commonly found in TMDs.

We study the (Mo,W)Te$_2$ system as a prototype. As shown in Figure 1, the 2H phase is trigonal prismatic, and 1T phase is octahedral. The monoclinic 1T' and orthorhombic T$_d$ are charge-ordered (i.e. lower-symmetry) variations of the 1T structure, for which in-plane isotropy is broken, and are crystallographically very similar. MoTe$_2$ is a semiconductor in the 2H structure in its ground state, and can be prepared as a semi-metal in the 1T' structure as a metastable state. WTe$_2$ is a semi-metal in the T$_d$ structure in its ground state, and could be a semiconductor in the 2H structure as a metastable state. The martensitic (i.e. displacive) phase transformation between 2H and 1T structures can be described by a lateral translation of one plane of chalcogen atoms.$^{18}$ This diffusionless, order-order transformation is expected to be faster, require less energy, and to cause less fatigue than melt-quench and recrystallization transformations needed for GST. Phase-change functionality at room-temperature has been demonstrated recently for MoTe$_2$ and (Mo,W)Te$_2$. The energy (i.e. enthalpy at 0 K) difference between 2H and 1T' phases of MoTe$_2$ is 40 meV per formula unit (f.u.); for WTe$_2$, the energy difference between the 2H and T$_d$ phases is -90 meV/f.u.$^{22}$ Making an alloy of MoTe$_2$ and WTe$_2$ decreases the energy difference between the 2H and distorted phases, and presumably reduces the energy barrier for switching.$^{22}$

Figure 1: Top and side views of TMD crystal polymorphs: 2H (a), 1T (b), 1T' (c) and T$_d$ (d).
Here we study MoTe$_2$ and Mo$_{0.91}$W$_{0.09}$Te$_2$, which both have 2H phase as the ground state and 1T$'$ phase as an excited, metastable state which can be experimentally-prepared. We measure the complex refractive index ($n + ik$) of 1T$'$-MoTe$_2$, 2H-MoTe$_2$, 1T$'$-Mo$_{0.91}$W$_{0.09}$Te$_2$ and 2H-Mo$_{0.91}$W$_{0.09}$Te$_2$ single crystal samples in the UV-to-NIR spectral range by spectroscopic ellipsometry (SE), and the normal-incidence reflectance by Fourier transform infrared spectroscopy (FTIR) microscopy. Our results show that the polymorphs of MoTe$_2$ and Mo$_{0.91}$W$_{0.09}$Te$_2$ have strong optical contrast in the NIR, and therefore may find use as phase-change materials for photonics. The loss coefficient of tellurium-based TMDs is rather large though, which motivates continued research on selenide and sulfide phase-change TMDs.

2. EXPERIMENTAL DETAILS

2.1. Crystal Growth

We synthesized 1T$'$- and 2H-Mo$_{1-x}$W$_x$Te$_2$ crystals, $x = 0$ and 0.09, using the chemical vapor transport method. First, we synthesized polycrystalline Mo$_{0.9}$W$_{0.1}$Te$_2$ powders by reacting appropriate amounts of Mo (99.999 %), W (99.9 %) and Te (99.9 %) at 750 °C in a vacuum-sealed quartz ampoule. Next, we grew Mo$_{0.9}$W$_x$Te$_2$ crystals at 950 °C using $\sim$1 g of polycrystalline Mo$_{0.9}$W$_x$Te$_2$ and a small amount of I$_2$ transport agent (99.8 %, 5 mg/cm$^3$) sealed in evacuated quartz ampoules. We quenched the samples in ice water after 7 days of growth, yielding Mo$_{0.9}$W$_x$Te$_2$ crystals in the semi-metallic 1T$'$ phase. We applied the same procedure to obtain 1T$'$-MoTe$_2$ crystals. 1T$'$-Mo$_{0.91}$W$_{0.09}$Te$_2$ crystals were converted to the semiconducting 2H phase by annealing in vacuum-sealed ampoules at 950 °C for 72 h, followed by cooling to room temperature at a 10 °C/h rate. We obtained the 2H-MoTe$_2$ crystals used in this study by chemical vapor transport growth at 800 °C for 140 h using TeCl$_4$ (99.9 %, 5.7 mg/cm$^3$) as a vapor transport agent.$^{20}$ We determined crystal phase and tungsten content using X-ray diffraction, Raman spectroscopy and energy-dispersive X-ray spectroscopy, respectively (not shown).

All the samples are thin, single-crystalline flakes about few millimeters wide and about tens of micrometers thick. The smooth, mirror-like facets available for optical characterization vary from tens to hundreds of micrometers wide. The samples are highly-anisotropic due to the layered, van der Waals-bonded crystal structure. The 2H phase is birefringent. The 1T$'$ and T$_d$ phases are technically trirefringent, due to broken in-plane symmetry. However, the charge-ordered domains are too small to be detected by the techniques used here, and may be irrelevant to many applications in integrated photonics; in other charge-ordered TMDs TaS$_2$ and TaSe$_2$, domains are on the nanometer-scale.$^{23,24}$ Therefore, we discuss all samples as if they are birefringent, with the ordinary optic axis (i.e. c-axis) perpendicular to the surface.

2.2. Ellipsometry

We performed spectroscopic measurements in UV-to-NIR spectral range ($\lambda = 300 - 2100$ nm) using a Woollam UV-NIR Vase Ellipsometer with focusing optics (spot size $\sim$300 μm). Ellipsometry is a non-destructive optical technique, widely used to measure the optical constants of thin films and bulk crystals.$^{25,26}$ The technique involves measuring the ellipsometric ratio ($\rho$) of the p- and s-polarized component of reflection Fresnel coefficients ($r_{pp}$, $r_{sp}$, $r_{ps}$, $r_{ss}$) on a smooth surface. A general form of the reflection matrix can be defined by the Jones matrix (S):

$$S = \begin{bmatrix} r_{pp} & r_{ps} \\ r_{sp} & r_{ss} \end{bmatrix} = r_{ss} \begin{bmatrix} \rho_{pp} & \rho_{ps} \\ \rho_{sp} & 1 \end{bmatrix}$$

(1)

where the cross-polarization components $\rho_{ps}$ and $\rho_{sp}$ are 0 for uniaxial samples. $\rho$ ($\rho_{pp}$, we drop the subscript for convenience) is measured as

$$\rho = \frac{r_{pp}}{r_{ss}} = \tan(\psi) \exp(-i\Delta)$$

(2)

where $\psi$ and $\Delta$ are the ellipsometric angles. $\rho$ is a complex function of the wavelength. For a simple device structure, $\rho$ completely determines the complex optical constant.

For a bulk, isotropic material the refractive index $n$ can be calculated directly from ellipsometric data as
\[ \epsilon = \sin^2(\Phi) \cdot \left(1 + \tan^2(\Phi) \cdot \left(\frac{1-p}{1+p}\right)^2\right) \]  

(3)

where \( \epsilon = \epsilon_1 + i \epsilon_2 \), and \( \Phi \) is the angle of incidence (AOI) relative to the surface normal direction\(^{25}\). \( \epsilon \) calculated using Equation 3 for anisotropic samples is called the "effective" permittivity and corresponds to a model of a pristine material interface with air. For ellipsometry measurements on the basal plane of TMDs, the large refractive index refractions the probe beam into near-normal orientation for all typical AOI values, and as a result the effective permittivity corresponds very closely to the in-plane permittivity\(^{27}\). We measure our samples as-grown, with no surface processing steps. (Mo,W)Te\(_2\) crystals have a self-limited native oxide, under 1 nm in thickness, the presence of which does not substantially affect the determined optical constants.

2.3. Reflectivity

We used an FTIR microscope (Bruker Lumos) to measure normal-incidence reflectance in the IR (\(\lambda = 1.3 - 16.6\) \(\mu m\)). The reflectance \( (R) \) depends on the in-plane, ordinary refractive index \( (n_o + ik_o) \) as

\[ R = \frac{(n_o-1)^2 + k_o^2}{(n_o+1)^2 + k_o^2}, \]  

(4)

The reflectance is real-valued number in the range \([0, 1]\), and cannot determine the in-plane complex refractive index without further modeling and/or Kramers-Kronig inversion. FTIR therefore contains less direct information about the optical material properties than ellipsometry. However, FTIR measurements are possible on more diverse samples, with smaller mirror-smooth regions (analysis spot size down to 50 \(\mu m\) on our instrument), and the data are directly relevant to applications of phase-change materials for optical data storage, and these attributes make FTIR a useful complementary technique to ellipsometry.

Equation 4 assumes that the sample is infinitely-thick, and the reflections from the back surface are non-existent. This assumption works well for semi-metallic 1T' samples with high absorption. However, the 2H samples are less than 100 \(\mu m\) thick, the FTIR measurements extend to \(\lambda = 16.6\mu m\), and the semiconducting phase is not strongly absorbing below-band gap. Therefore, backside reflections in the semiconducting 2H samples result in substantial oscillations in the reflectivity data. To make a clear comparison between the reflectivity data for 2H and 1T' samples, highlighting the intrinsic material properties and not the sample dimensions, we used numerical modeling to remove the oscillations from the data. We used a model of a Lorentzian dielectric media of finite-thickness to fit the data, and we then re-plotted the model predictions for an infinitely-thick sample according to Equation 4.

![Figure 2: NIR-UV complex effective refractive index of 1T' (a) and 2H (b) MoTe2. Measured at room-temperature and AOI = 70° by spectroscopic ellipsometry.](Image)


3. Results and Discussion

In Figure 2 we present the complex refractive indices of MoTe$_2$ in the 2H and 1T’ phases, measured by ellipsometry. Both phases have high $n$, indicating strong dielectric polarizability at optical frequencies. 1T’-MoTe$_2$ has high loss coefficient throughout, as expected for a semimetal. It may be expected to have negative $n$ at low energy, below the plasma edge, but our data do not extend into this region. As a semiconductor, 2H-MoTe$_2$ has suppressed loss below its band gap of 1.0 eV$^{28}$. The spectral features that we measure for 2H-MoTe$_2$ match those previously reported by others. The A, B, A’, and B’ excitons (at 1.1, 1.4, 1.7, and 2.0 eV, respectively) that are split by spin-orbit and interlayer interactions are well-resolved, as are the C and D excitons (at 2.5 and 2.9 eV, respectively) that result from parallel band near the Brillouin zone Γ-point$^{28}$.

Figure 3: Δ$n = n_{2H} - n_{1T'}$ and phase-change figure of merit, FOM = |Δ$n$|/(k$_{2H}$ + k$_{1T'}$) for MoTe$_2$.

In Figure 3 we present the difference between refractive indices of 2H- and 1T’-MoTe$_2$, Δ$n = n_{2H} - n_{1T'}$. The large and variable data for $n$ results in Δ$n ∼ σ(1)$. The prospects for phase-change performance can be captured by the figure-of-merit FOM = |Δ$n$|/(k$_{2H}$ + k$_{1T'}$), and the large Δ$n$ demonstrated here is promising. However, both phases are quite lossy, which suppresses the FOM to the range 0.4-0.9 the NIR bands most relevant for communications (1000 – 1550 nm).

In Figure 4 we present the reflectance of 1T’ and 2H phases of MoTe$_2$ and Mo$_{0.91}$W$_{0.09}$Te$_2$ in the range 0.05-0.9 eV, measured by FTIR microscopy. The semi-metallic 1T’ phases have higher reflectivity than the semiconducting 2H phases, as expected. The strong optical contrast between phases persists even as the thermodynamic barrier decreases with alloying.
Figure 4: IR reflectance of 2H and 1T’ MoTe$_2$ (a) and Mo$_{0.91}$W$_{0.09}$Te$_2$ (b) measured by FTIR microscopy. For the 2H-phase samples, the reflectance data has been corrected to account for backside reflection.

4. CONCLUSION

We use the (Mo,W)Te$_2$ system to explore the potential of TMDs as phase-change materials for integrated photonics. We measure the complex optical constant of MoTe$_2$ in both the 2H and 1T’ phases by spectroscopic ellipsometry. We find that both phases have large refractive index, which is good for confined light-matter interaction volume. The change $\Delta n$ between phases is of $\mathcal{O}(1)$, which is large and comparable to established phase-change systems such as GST. However, both phases have large optical loss, which limits to FOM to below unity throughout the measured range. We further measure the NIR reflectivity of MoTe$_2$ and Mo$_{0.91}$W$_{0.09}$Te$_2$, in both the 2H and 1T’ phases. The data show that the strong optical contrast between the 2H and 1T’ structures persists even as the thermodynamic barrier between them is reduced by alloying. This bodes well for alloy design of phase-change materials.

Our results emphasize that TMDs have strong light-matter interaction, a number of polymorphs with strong optical contrast, and chemical diversity. The tellurium-based TMDs reported here have demonstrated phase-change operation, and may be relevant for applications including resistive memory and analog computing$^{20}$. We suggest that selenium- and sulfur-based TMDs may be optimal for photonic phase-change applications because they are expected to have lower loss.
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