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1T-TaS$_2$: A strongly correlated material for tunable nanophotonics

by

Weijian Li

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APPROVED, THESIS COMMITTEE:

Gururaj V. Naik, Chair
Assistant professor of Electrical and Computer Engineering

Kevin F. Kelly
Associate Professor of Electrical and Computer Engineering

Jun Lou
Professor of Materials Science and NanoEngineering

Junichiro Kono
Professor of Electrical and Computer Engineering, Physics and Astronomy, Materials Science and Nanoeengineering

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ABSTRACT

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Tunable nanophotonics have been demonstrated for several decades and achieved to practical applications in real world in multiple ways such as imaging, sensing, signal processing, information communication and etc. Many different mechanisms have been involved in such modulating, gate tunable Fermi energy of graphene, MEMS devices, chemical reaction. However the tunabilities of all of mechanisms are either small or slow due to small capacitive gaps and large stimulus. Fortunately materials with especially electric tunable optical properties are supposed to be one of the solution for overcoming this limitation. Hence, tunable optical materials are attracting more interests and under deeply investigations.

Strongly correlated materials provides a group of candidates for tunable optical materials in which electronic and phononic structures are strongly sensitive to external environments. Transition Metal Dichalcogenide (TMDs), a prototype of two-dimensional (2D) compound, is one of the well studied strongly correlated materials exhibiting numerous different interesting phases such as superconducting, charge density wave (CDW) and spin liquid from liquid Helium temperature to above room temperature. Some of them even exhibit non-Fermi liquid behaviors raised from strongly interaction among localized sub-shell electrons of transition metals atoms. Because of the diverse phase transitions and non-Fermi liquid properties, TMDs pro-
vide possible larger tunabilities of optical properties of the materials compared with normal semiconductors.

Although optical properties of materials hugely differ around phase transition point, low temperature makes almost all of them hard be implemented in dynamic world optical applications. CDW is one of the quantum ground states that can happen around room temperature which makes the host materials possible platforms for tunable nanophotonic applications. This quantum phase is a result of strong interaction between electrons and phonons of the materials producing a condensate that rearranges the lattice and produces a nested Fermi surface. Many TMDs support charge density waves such as NbSe$_2$ and TiSe$_2$, but 1T-TaS$_2$ supports CDWs at room temperatures which attracts increasing interests of physicists due to its non-equilibrium state that can be excited by electric field and light.

In this thesis, we propose that 1T-TaS$_2$ is a promising candidate for tunable nanophotonics due to its tunable optical properties in visible by in-plane electric bias and therm-optical effect. We demonstrate that the refractive index can be tuned up to 0.1 in visible at room temperature by both DC and AC in-plane bias and up to 0.4 by white light excitation. By implementing this tunability of optical properties of 1T-TaS$_2$, we theoretical propose a grating design that shift the first diffraction angle at 516 nm by $15.4^\circ$ under 2.5 mW/cm$^2$ and 250 mW/cm$^2$ white light excitation. Finally we experimentally vary this application of 1T-TaS$_2$ by showing up to 1 nm diffraction peak shift at around 558 nm.
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Chapter 1

Introduction

Dynamically tunable nanophotonic devices are necessary for many applications including imaging, displays, and information processing [1–3]. Electrical tunability is preferred in many of these applications as it allows easy integration with control electronics. Electrically tunable optical materials form the core of such devices where small change in optical constants of the material can produce a large change in the overall functionality. Many such solid-state materials have been investigated before for visible and near-infrared applications, e.g., semiconductors [4,5], transparent conducting oxides [6,7], graphene [8,9], MEMS devices [10] and thermal phase change materials such as chalcogenide glass [11]. However, their tunability is either small or require large stimulus. In the case of field-effect tunable materials, large stimulus is also not an option due to the limitation of electrical breakdown in the capacitive gap. In an attempt to overcome this limitation, here in this thesis, we report a new class of material for such electrically tunable applications requiring only an in-plane bias. We study the electrically tunable optical properties of 1T-TaS$_2$, a quasi 2D material that exhibits strong correlation of charge density order [12].

1.1 Tunable nanophotonics

Due to the development of nano structure fabrication technique, nanophotonics has experienced a fundamental breakthrough and exhibits potential possibilities of dis-
ruptive applications in real world. Tunable nanophotonics is a study that precisely manipulates light by using metallic and dielectric nanostructures in which light can be scattered, absorbed, refracted, confined which can not be achieved with natural materials and in macro scale geometries. It shrinks light in sub-wavelength scale that the lateral sizes of isolate structures of photonic devices are smaller than the wavelength of excited light, involving many basic physics principles such as plasmonics, photonic crystals, Mie resonance, metamaterials and metasurfaces depending on the materials used in the systems. If the responses of nanophotonic devices are dependent to any external perturbations e.g. temperature, humidity, pH circumstance or geometry, such systems are tunable and more likely to applied in practice.

Until now, many tunable nanophotonic applications have been achieved in real world such as imaging, sensing, optical modulator, energy serving and etc. However, none of each mechanism satisfies the requirements of real application because of the lack of either large or fast tunability. In attempt to overcome such a limitation, electronically tunable optical materials whose optical properties are sensitive to local electric field around room temperature are attracting increasing interests by researchers. By controlling the intrinsic optical properties of materials making up of nano devices by electric fields, the amplitude and phase of excited light can be precisely tailored.

### 1.2 Strongly correlated materials

It is well know of Drude-Lorentz model describing the optical properties of normal metal and semiconductors very well as shown in Equ 1.1.

\[
\varepsilon_r(\omega) = \varepsilon(\infty) - \frac{\omega_p^2}{\omega^2 + j\omega\Gamma} + \omega_p^2 \sum_n \frac{f_n}{\omega_m^2 - \omega^2 - j\omega\Gamma_n} \tag{1.1}
\]
where $\varepsilon(\infty)$ is the permittivity at infinite frequency, $\omega_p$ is plasma frequency, $\Gamma_n$ are the damping coefficients, $\omega_n$ are resonant frequencies and $f_n$ is the oscillators strength factor. Drude-Lorentz model considers the contributions of optical properties from both free carriers and interband transitions and works well for almost all of Fermi gas or Fermi liquid system in which electrons can be treated as single particles. However, such model collapses in non-Fermi liquid systems such as superconductor and CDW materials which provide a possibility to break the limitation of Drude-Lorentz model. Nevertheless, non-Fermi liquid systems also usually have a relative large non-linear behavior due to strongly response of collective modes of electrons as shown in Tab. 1.1.

Table 1.1 : Non-linear optical coefficient of semiconductors

<table>
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<tr>
<th>Materials</th>
<th>$n_0$</th>
<th>$\chi^{(3)}$ (cm$^2$/V$^2$)</th>
<th>$n_2$ (cm$^2$/W)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diamond</td>
<td>2.42</td>
<td>$21 \times 10^{18}$</td>
<td>$10 \times 10^{16}$</td>
</tr>
<tr>
<td>Sapphire</td>
<td>1.83</td>
<td>$8.4 \times 10^{18}$</td>
<td>$8.4 \times 10^{16}$</td>
</tr>
<tr>
<td>Fused silica</td>
<td>1.47</td>
<td>$2.8 \times 10^{18}$</td>
<td>$3.67 \times 10^{16}$</td>
</tr>
<tr>
<td>CaF$_2$</td>
<td>1.43</td>
<td>$2.24 \times 10^{18}$</td>
<td>$3.1 \times 10^{16}$</td>
</tr>
<tr>
<td>monolayer MoS$_2$</td>
<td>5.3</td>
<td>$\sim 10^{15}$</td>
<td>$\sim 1.7 \times 10^{13}$</td>
</tr>
</tbody>
</table>

Values are obtained at not necessary same certain wavelengths for each materials [13,14]

Strongly correlated materials usually exhibit non-Fermi liquid as well as heavy Fermion properties. The electrons in such materials interact to each other by different mechanisms, e.g. exchanging phonons (CDW and superconductor), on-site repulsion (Hubbard model), spin interaction (ferromagnetic, anti-ferromagnetic, spin-liquid) and
etc. Due to the strongly interactions of electrons, the matter light interactions are no longer the results of single particle interactions, leading to significant enhancement as the energy and momentum absorbed by electrons from photons would disperse into other electrons quickly.

1.3 Transition metal dichalcogenides

Transition metal dichalcogenides (TMDs), which are usually semiconductor at room temperature of type MX$_2$ where M is transition metal element (e.g. Mo, W or Ta) and X is chalcogen element (e.g. S, Se or Te), exhibit multiple novel physical phenomena making them highly attractive for fundamental studies and applications in nanoelectronics and nanophotonics. It has been a long and colorful history of TMDs since the first time of determination of lattice structure of MoS$_2$ in 1923 by Linus Pauling [15]. Until now, around 60 TMDs have been known as well as their optical properties and used in various photonic applications.

There are two most common structural phases, trigonal prismatic (2H) and octahedral (1T) phases characterized by the coordinations of transition metal atoms as shown in Fig. 1.1. In terms of stacking configuration of three-atom-planes, 2H phases correspond to ABA stacking while 1T phases correspond to ABC stacking. From the top view of lattice order of 2H phases, the chalcogen atoms in top layer and bottom layer are overlap so that honey cone lattice shape emerges. While in 1T phase, the chalcogen atoms in two layers are mismatch. Thermodynamically stable phase of TMDs could be 1T, 2H or some other phases depending on the combination of transition metal and chalcogen atoms, which might have totally different physical properties. For example, $1T'$ phase of MoTe$_2$ and WTe$_2$ are supposed to be Wely semimetal candidates.
Figure 1.1: Lattice structure of transition metal dichalcogenides in trigonal prismatic (2H), octahedral (1T) phases. Up half: top view, down half: side view.
Although many TMDs exhibit different thermodynamic ground states such as metallic, semiconductor, superconducting, topological as shown a 'Periodic table' in Fig 1.2, CDW phase is attracting more interests due to its room temperature and the similar fundamental physics with superconductors [16]. CDW phases have been discovered in both 1T and 2H phases of TaS\textsubscript{2} and TaSe\textsubscript{2} and 2H-NbSe\textsubscript{2} in TMDs. For example, 1T-TaS\textsubscript{2} undergoes a nearly commensurate CDW ($\lambda_{CDW}$ is not but nearly an integer multiple of the lattice constant) to incommensurate CDW phase transition at around 350 K, resulting in a David-star periodic lattice disorder modulation with $\sqrt{13} \times \sqrt{13}$ periodicity. Our thesis is attempt to investigate the optical properties of 1T-TaS\textsubscript{2} and more details will be discussed in chapter 3.

Figure 1.2 : 'Periodic table' of known TMDs including both 2H and 1T phases. Possible electronic phases are indicated in each square of elements, where 'dis' represents distorted phase, 'M' represents metallic phase, 'I' represents insulating phase, 'CDW' represents charge density wave phase, 'SC' represents superconducting phase and 'Topo' represents topological phase.
Chapter 2

Charge Density wave

This chapter will provide a brief introduction of charge density wave, including the basic physics principle, pinning mechanism and a simple model for CDW.

2.1 Introduction of CDW

Charge density wave was first time pointed out by Peierls in 1955 that there is no metallic ground state in any one-dimensional systems at zero temperature. After about 20 years, the first CDW material was found of NbSe$_3$ with 1D chain crystal structure by detecting longitudinal resistivity anomalies at 145 K and 58 K in 1976 [17]. Until now, many CDW materials have been demonstrated including inorganic and organic, 1D and 2D systems such as K$_{0.3}$MoO$_3$, TTF-TCNQ, NbSe$_2$, and 1T-TiSe$_2$. CDW phenomenon is a result of strong interaction between electrons throung exchanging phonons of the material on Fermi surface, producing a condensed mode of electrons that periodically rearrange the lattice and open a gap at Fermi surface. Many unique effects are caused by CDW phase including non-linear DC conductivity, high dielectric function, modulated current noise, periodic lattice disorder, amplitude mode excitation and etc. More details will be discussed below.
2.2 Peierls theory

Peierls pointed out in 1955 that there is no metallic ground state in any 1D system at zero temperature. Let’s consider a 1D metal whose valance band is half filled indicating a metallic state, as shown in Fig. 2.1a. This configuration of electronic system is not energetic favorable because of the lower energy of electrons by doubling the lattice constant and opening an gap at Fermi surface as shown in Fig. 2.1b. The lattice distortion introduces a modulation in wave form of charge density in free space with period $\lambda_{CDW}$ related to the Fermi wave vector by

$$\lambda_{CDW} = \frac{\pi}{k_F} \quad (2.1)$$

Rice and Strässler proved in 1973 that in one dimensional system, the single-particle gap opened by lattice distortion is proportional to the amplitude of the periodic lattice disorder $u$, leading to the decrease of the electronic energy is proportional to $u^2 \ln u$. While the increase of the elastic energy caused by the distortion is proportional to $u^2$ [12]. As a result, for any finite distortion, the total energy of the system is smaller than the undistorted metallic one, indicating impossibility of 1D metals.

Peierls theory can be understood more clearly as considering the Hamiltonian with electron-phonon interaction as shown in Equ. 2.2, Equ. 2.3 and Equ. 2.4.

$$H_{el} = \sum_{k,\sigma} \epsilon_k a_{k,\sigma}^\dagger a_{k,\sigma} \quad (2.2)$$

where $\epsilon_k = \hbar^2 k^2 / 2m_e$ is the energy dispersion of electrons, $a_{k,\sigma}^\dagger$ ($a_{k,\sigma}$) are the creation (annihilation) operators for electrons with momentum of $\hbar k$ and spin of $\sigma$. 
Figure 2.1: Peierls distortion in a 1D atomic chain with half filled band structure: (a) 1D metal without distortion; (b) Peierls insulator. $\rho(r)$ is the density of charge in real space which has wave form for the first order approximation in Peierls insulator.
\[ H_{\text{ph}} = \sum_q \frac{P_q P_{-q}}{2M} + \frac{M \omega_q^2}{2} Q_q Q_{-q} \]
\[ = \sum_q \hbar \omega_q \left( b_q^\dagger b_q + \frac{1}{2} \right) \]  
(2.3)

where \( \omega_q \) is the quantum frequency of phonons, \( b_k^\dagger (b_k) \) are the creation (annihilation) operators for phonons.

\[ H_{\text{el-ph}} = \sum_{k,k',R} \langle k | V (r - R - u) | k' \rangle a_k^\dagger a_{k'} \]
\[ = \sum_{k,k',R} e^{i(k' - k)(R + u)} V_{k' - k} a_k^\dagger a_{k'} \]  
(2.4)

where \( V_{k' - k} \) is Fourier component of atomic potential \( V(r) \), \( R \) is the lattice position in equilibrium state, \( u \) is the ions displacement and \( |k\rangle = \frac{1}{\sqrt{L}} e^{ikr} \). We assume that the interactions between electrons and phonons only depend on the distance from the center of atom. If the displacements are small, we can expand the exponential term:

\[ e^{i(k' - k)u} \approx 1 + iu (k' - k) = 1 + \frac{i}{\sqrt{N}} (k' - k) \sum_q u_q e^{iqR} \]  
(2.5)

Again using second quantization:

\[ H_{\text{el-ph}} = \frac{i}{\sqrt{N}} \sum_{k,k',R,q} e^{i(k' - k + q)R} (k' - k) u_q V_{k' - k} a_k^\dagger a_{k'} \]
\[ = i \sqrt{N} \sum_{k,k'} (k' - k) u_{k-k'} V_{k' - k} a_k^\dagger a_{k'} \]
\[ = \sum_{k,q} g_q (b_{-q}^\dagger + b_q) a_k^\dagger a_k \]  
(2.6)

where the electron-phonon coupling constant is

\[ g_q = i \left( \frac{\hbar}{2M \omega_q^2} \right)^{1/2} |q| V_q \]  
(2.7)
Thus we get the so-called Frolich Hamiltonian:

\[
H = \sum_{k,\sigma} \epsilon_{k,\sigma} a_{k,\sigma}^\dagger a_{k,\sigma} + \sum_{q} \hbar \omega_q \left( b_q b_q + \frac{1}{2} \right) + \sum_{k,q} g_q \left( b_{-q}^\dagger + b_q \right) a_{k}^\dagger a_{k} \tag{2.8}
\]

Now defining a complex order parameter by using mean-field theory

\[
\Delta^{i\phi} = g_{q=2k_F} \langle b_{2k_F} + b_{-2k_F}^\dagger \rangle \tag{2.9}
\]

where \(\Delta\) and \(\phi\) are two real parameters (gap equation). Now we can draw a schematic for the total energy of the system in terms of the order parameter. The minimum energy cross section in metallic phase has a zero amplitude order parameter as well as a zero band gap as shown in Fig. 2.2a. While in CDW phase, the energetic favorable complex order parameter has a finite amplitude but total 2\(\pi\) phase forming a circle cross section as shown in Fig. 2.2b. By distorting the dispersion relation, there are two collective modes for electrons could be excited in CDW system. Phase mode (Goldstone mode), called phason, is a gaplessed mode if the order parameter varies along minimum energy circle cross section involving no energy perturbation. While amplitude mode (Higgs mode) is a gaped mode if the order parameter oscillates around the minimum energy state, making it hard to be excited.

### 2.3 Pinning mechanism

Differing to normal metal, impurities play an significantly important role in CDW system. Many unique phenomena in CDW materials are related to such mechanism including non-linear conductivity, high dielectric function, current oscillations and etc. In order to understand the pinning effect in CDW systems, let’s consider a Hamiltonian with impurities pinning potential [18]
Figure 2.2: Total energy dispersion of system in terms of complex order parameter $\Delta e^{i\phi}$ in a) metallic phase, b) CDW phase. The minimum energy cross section in metallic phase has a zero amplitude order parameter. While in CDW phase, the energetic favorable complex order parameter has a finite amplitude but total $2\pi$ phase forming a circle cross section. There are two collective modes for electrons in CDW system: gapless phase mode (Goldstone mode) and gaped amplitude mode (Higgs mode).

\[
H = \frac{n_c \hbar v_F}{4\pi} \int (\nabla \phi)^2 \, dr + \int \rho_1 V(r) \cos [2k_F \cdot r + \phi(r)] \, dr \quad (2.10)
\]

where $n_c = \frac{e}{\pi} \frac{d\phi}{dr}$ is the density function of CDW, $v_F$ is the Fermi velocity. Here we assume the displacements of amplitudes of collective mode can be ignored compared with phase perturbed by the interaction between charge wave and pinning potential $V(r)$. The right-hand side includes two terms: elastic energy generated by long-wavelength phase deformations and the interaction of the phase mode with the pinning potential. For small phase displacements approximation, the pinning energy is given by

\[
E_{pin} = \frac{K \lambda_{CDW}^2}{8\pi^2} (\phi - \phi_0)^2 \quad (2.11)
\]
where K is the spring constant. By the definition of pinning potential, the collective mode cannot translating move unless the DC electric field exceeds a threshold field $E_T$. Defining a pinning frequency $\omega_0^2 = K/m^*$, the threshold field is given by

$$E_T = \frac{\lambda_{CDW} K}{2e} = \frac{\lambda_{CDW} m^* \omega_0^2}{2e}$$  \hspace{1cm} (2.12)$$

Now the current carried by both free carriers and condensed charge density wave is given by:

$$\langle J \rangle = \begin{cases} \sigma_0 E, & E < E_T \\ \sigma_0 E + \frac{n_c d^2 \tau}{m^*} (E^2 - E_T^2)^{1/2}, & E > E_T \end{cases}$$  \hspace{1cm} (2.13)$$

Here $\sigma_0$ is the DC conductivity for free carriers. Natural CDW materials exhibit non-linear DC conductivities with much smaller threshold electric field compared with normal semiconductors. A semi-empirical equation Eq. 3.1 [12] is usually used to capture the non-linear DC conductivity of CDW systems, which will be discussed in Sec. 3.3.

Moreover, the high dielectric functions of CDW materials are also arised from the pinning effect. Considering the time and position dependence of the phase $\phi(x, t)$, the motion equation of collective mode in the presence of an applied ac field with frequency $\omega$ is given by:

$$\frac{d^2 \phi}{dt^2} + \frac{1}{\tau} \frac{d\phi}{dt} + \frac{m}{m^*} \frac{v_F^2}{dx^2} \frac{d^2 \phi}{dx^2} = \frac{2k_F e E(\omega)}{m^*}$$  \hspace{1cm} (2.14)$$

indicating a collective mode resonance around $\omega_0^2 = \sqrt{\frac{m^*}{m^*}} \frac{e\omega}{\hbar}$. A schematic of frequency dependent optical conductivity with impurities pinning effect and damping is shown in Fig. 2.3. The optical conductivity above the resonance frequency $\omega_0$ is due to single particle response.
Figure 2.3: Frequency dependent optical conductivity with impurities pinning potentials. The optical conductivity above the resonance frequency $\omega_0$ is due to single particle response.

2.4 ‘Single particle’ model

A classical ‘single particle’ model is implemented to understand pinning effect in CDW system as shown in Fig. 2.4. The ‘particle’ representing the collective mode of electrons cannot roll out of the sinusoidal pinning potential well for small DC fields unless the field exceeds a threshold $E_T$, leading to non-linear DC conductivity of CDW materials. For small AC field, the ‘particle’ oscillate in the potential well and resonant with frequency $\omega_0$ as derived before.
Figure 2.4: ‘Single particle’ model of CDW transport properties for: a) dc and b) ac field. The particle represents the collective mode of electrons. Assuming impurities pinning potential is sinusoidal function of $\phi$. 
Chapter 3

Room temperature CDW: 1T-TaS$_2$

Many materials supporting charge density waves such as NbSe$_3$, TaS$_3$, and TiSe$_2$, exhibit strong correlation and CDW at low temperatures [19]. However, 1T-TaS$_2$ supports CDWs at room temperatures [20]. 1T-TaS$_2$ shows two phase transitions at 190 K and 348 K, separating three states: commensurate charge density wave (CCDW), near commensurate CDW (NCCDW) and incommensurate CDW (IC-CDW) states [21] depending on the extent of lattice reorganization or condensation. The transition between NCCDW and ICCDW phases of 1T-TaS$_2$ above room temperature results in its extreme sensitivity to light [22], electrical bias [23] and temperature [24] making it a promising candidate for tunable nanophotonics.

Though previous demonstrations have shown that 1T-TaS$_2$ exhibits nonlinear conductance at room temperature [25], hysteresis behavior of electric resistance [21] and its phase transition that can be tuned by pressure [26], strain [27], thickness [28], gate voltage [29], and chemical doping [30,31], its optical properties remain unexplored. In this chapter 3, we provides an overview of 1T-TaS$_2$ and a discuss of our research on this material’s optical properties in details. Finally, we provide a theoretical prediction of a meta-grating device and experimentally show the tunability of such device.
3.1 CDW phenomenon of 1T-TaS$_2$

In 1T-TaS$_2$, three charge density waves phases have been experimentally reported in both bulk and two in monolayer [28]. As shown in Fig 3.1, DC resistivity of bulk 1T-TaS$_2$ shows two anomalies at ranging from 180 K to 220 K and at 350 K, corresponding two phase transitions [26]. A strong hysteresis effect is observed at CCDW to NCCDW phase transition and a weak one at NCCDW to ICCDW phase transition. In CDW phase of 1T-TaS$_2$, the lattice rearranges involving 13 Ta atoms forming a David-star structure as shown in Fig. 3.1 inset.

Figure 3.1: DC resistivity of bulk 1T-TaS$_2$ as a function of temperature. Two phase transitions are at around 200 K and 350 K. Hysteresis effects are obvious in 1T-TaS$_2$. The inset shows the crystal structure of a layer of 1T-TaS$_2$. When 1T-TaS$_2$ is in CDW phase, the Ta atoms on corners of the red star will move inwards making a 13-atom David-star cell.
3.2 Sample preparation and crystalline characterization

Pure 1T-TaS$_2$ crystals were purchased from 2D Semiconductors (www.2dsemiconductors.com). Thin films of 1T-TaS$_2$ were obtained from bulk single crystals using mechanical exfoliation and subsequent transfer to substrates. Glass cover slides were chosen to be substrates due to their transparency in the visible spectrum. Thickness of 1T-TaS$_2$ after exfoliation were measured by Atomic Force Microscope (AFM) and profilometer. The material quality of the sample was characterized by X-Ray diffraction (XRD) and Raman spectra. Cu K-$\alpha$ X-ray line is used for XRD, while a 532 nm wavelength CW laser was used for Raman scattering measurement.

The as-exfoliated 1T-TaS$_2$ films showed single crystalline characteristics as seen from XRD plot of Fig. 3.2a. The four peaks at 14.99°, 30.26°, 46.13° and 62.97° correspond to 001, 002, 003 and 004 crystal planes respectively [32, 33]. Six X-Ray diffraction peaks at around 45° as seen in Fig. 3.2b in 360° rocking angle plot indicate 1T phase (hexagonal lattice) of our sample. Further, the crystal phase of the films was identified by Raman scattering spectra of Fig. 3.3. The Raman shifts at 254 cm$^{-1}$, 306 cm$^{-1}$ and 379 cm$^{-1}$ indicate lattice disorder of TaS$_2$ [34].

3.3 1T-TaS$_2$ transport properties characterization

The electrical characterization of the exfoliated films were carried out using in-plane bias across the contacts prepared. Electron beam lithography and electron beam evaporation were used to make top electrodes after exfoliation as shown in Fig. 3.3b inset. DC and ac measurements were carried out using Keithley 2450 SMU and HF2LI from Zurich Instruments. Only DC transport measurements were carried out using a pulsed current source to avoid Joule heating in the sample, and rest all with unmod-
Figure 3.2: Material properties of exfoliated 1T-TaS$_2$ films: a) X-ray diffraction plot of 1T-TaS$_2$ showing four peaks corresponding to the planes indicated. b) Six diffractive peaks in half sphere X-ray scan at around 45° indicating hexagonal lattice with $a/c \approx 0.57$. c) Raman spectrum of exfoliated 1T-TaS$_2$ using 532 nm laser excitation.
ulated sources. The modulated DC current source for transport measurements had 1 ms pulse duration and 4 s period and was observed to cause negligible temperature rise.

\[ \sigma(E) = \sigma_\infty \left(1 - \frac{E_T}{E}\right) \exp\left(-\frac{E_0}{E}\right) \]  

(3.1)

The measured DC conductivity of as-exfoliated 1T-TaS\(_2\) film is shown in Fig. 3.3a along with the theoretical estimate for a film with a depinning threshold \(E_T = 10\) V/cm.
and $E_0 = 83$ V/cm. [25]. The non-linear DC conductivity confirms the presence of condensed CDWs in our 1T-TaS$_2$ film at room temperature. The measured magnitude of ac impedance of 1T-TaS$_2$ is shown in Fig. 3.3b. The impedance is almost a constant up to about 10 kHz and increases like an inductor. The kinetic inductance of condensed charge carriers is much higher than free carriers leading to a much smaller frequency of transition to inductive behavior.

### 3.4 1T-TaS$_2$ optical properties characterization

Optical characterization was carried out with low intensity excitation and a microscope coupled to an imaging spectrophotometer. The reflectance and transmittance were measured using an excitation source of ps-pulsed supercontinuum laser with a repetition rate of 2.24 MHz. All other optical measurements were carried out using a low intensity white light excitation from a tungsten-halogen lamp. The imaging setup used an objective with 0.45 NA and 10$\times$ magnification for all measurements except the angle dependent reflection. The angle resolved reflectances in TM and TE polarizations were measured using Fourier plane imaging technique through an oil-immersion objective of NA 1.45 and 100$\times$ magnification. The spectrum was collected by Princeton Instruments IsoPlane spectrometer and Pylon CCD. The resolution of the spectrometer was 0.2 nm and the estimated mean error in intensity measured is about 0.5%.

At first, we measure the normal incidence reflectance and transmittance spectra of as-exfoliated 1T-TaS$_2$ films at low intensity white light excitation without bias as shown in Fig. 3.4a for a film with an average thickness of 97 nm. Using these reflectance and transmittance spectra, the in-plane dielectric function ($\varepsilon_o$) of the 1T-TaS$_2$ film was extracted for every wavelength point and is plotted in Fig. 3.4b. In
Figure 3.4: Anisotropic optical properties of 1T-TaS$_2$ without any electrical bias: a) Normal incidence reflectance (left axis) and transmittance (right axis) spectra under low intensity white light excitation. b) Extracted real ($\varepsilon'$) and imaginary ($\varepsilon''$) permittivity functions in in-plane ($\varepsilon_o$) and out-of-plane ($\varepsilon_e$) directions. The out-of-plane permittivity function was extracted using angle dependent reflectance spectra measured in c) TE and d) TM polarizations.
the wavelength range of 540 to 840 nm, 1T-TaS$_2$ has both large real and imaginary
dielectric constants making it a lossy high index dielectric material.

Since this quasi-2D layered material should possess uniaxial anisotropy [35], the
dielectric function ($\varepsilon_c$) along c-axis or direction normal to layers is expected to be
different from the in-plane dielectric function, $\varepsilon_o$. Angle dependent reflection mea-
urements in both TE and TM polarization without bias, as shown in Fig. 3.4c and
d, were used to extract this c-axis dielectric function. Since only reflectance data was
available for the extraction of dielectric function, a Lorentzian model was assumed
for $\varepsilon_c(\omega)$ and is plotted in Fig. 3.4b.

3.5 In-plane electric bias tunable optical properties of 1T-TaS$_2$

Using the same optical measurement setup, we characterize the change in the optical
properties of the 1T-TaS$_2$ film with both DC and ac biases. With an in-plane DC
bias, the measured reflectance of 1T-TaS$_2$ film is as shown in Fig. 3.5a. Reflectance
monotonically decreases for wavelengths shorter than 700 nm with increasing bias
up until 1.5 V. However, when the in-plane bias reaches 2 V, the 1T-TaS$_2$ transits
from NCCDW to ICCDW phase resulting in a change in the shape of the reflectance
spectrum. The phase transition was confirmed by DC conductivity measurements
not shown here. We suspect that the observed changes in reflection are mainly due
to Joule heating of the sample though there has been some recent evidence of DC
bias reducing the phase transition temperature [36]. A simple estimation shows that
the minimum temperature rise expected in our film at 0.5 and 2 V DC biases are
about 2 and 20 K respectively. Thus, higher bias leads to higher temperatures which
in turn create more free carriers leading to larger plasma frequency. Higher plasma frequency results in larger reflection at longer wavelengths and smaller reflection at wavelengths shorter than the plasma wavelength, thus explaining the observed trend in Fig. 3.5a. The change in the reflection with bias plotted in Fig. 3.5a can be translated to a change in refractive index of the film. The projected change in the real index of the film is as shown in Fig. 3.5b. Maximum index change of about 0.1 is observed with an in-plane bias of 2 V. The bump in $\Delta n$ observed at around 570 nm could be due to interband transitions in ICCDW phase. The phase transition of 1T-TaS$_2$ from NCCDW phase to ICCDW phase would cause a reconfiguration of crystalline structure and change the electronic band structure [37].

![Graph](image)

Figure 3.5: DC bias dependent optical properties of 1T-TaS$_2$ films: a) Relative change in reflectance spectrum of 1T-TaS$_2$ at room temperature under in-plane DC bias from 0.5 V to 2 V, and b) Corresponding absolute change in real refractive index.

The CDWs in 1T-TaS$_2$ also respond to ac bias and hence are expected to exhibit frequency and amplitude dependent optical properties. Fig. 3.6 shows the measured changes in reflectance spectra of a near 125 nm thick film with different ac bias.
amplitudes at 1 MHz frequency. In contrast to the DC case, ac bias at 1 MHz causes
the reflectance to increase with increasing amplitude (see Fig. 3.6a). The ac bias
reinforces condensation of CDWs by causing them to slide and enhance coherence.
Thus, the ac bias reduces the number of carriers available for optical conduction and
hence increases reflectivity of the film. The initial decrease in reflectivity for 100 mV
bias could be due to Joule heating. However for larger biases, the effect of additional
Joule heating is negligible and the reflectance shows a monotonically increasing trend.
(Our estimates show that the minimum temperature rise at 500 mV, 1 MHz ac bias is
about 2.4 mK.) The corresponding change in real refractive index of the film is shown
in Fig. 3.6b. Except for 100 mV, all other curves show an increase in the index as
expected. The largest change in index observed here is about 0.06 though higher bias
amplitude can result in even larger change.

Similar to the ac bias amplitude, increasing frequency up to the saturation fre-
quency $\omega_p$ usually in MHz, can also result in increasing reflection and thus increasing
index [38]. The frequency dependence as shown in Fig. 3.6c for a constant amplitude
of 500 mV shows a monotonic trend of increasing reflectance with frequency. CDWs
are known to exhibit strong resonances in higher MHz frequency range and thus,
increasing frequency reinforces their condensation and thus the observed trend in the
reflectance. The corresponding change in real refractive index of the film is plotted in
Fig. 3.6d. Just by tuning the excitation ac frequency, the refractive index of 1T-TaS$_2$
films can be changed by about 0.06.

3.6 Tunable meta-grating device

Since the external perturbation such as electric field, temperature and optical exci-
tation influence the degree of condensation of carriers in 1T-TaS$_2$ [21, 23, 24], these
Figure 3.6: ac bias dependent optical properties of 1T-TaS$_2$ films: a) Relative change in reflectance spectra and b) absolute change of refractive index of 1T-TaS$_2$ for different amplitudes of ac bias at 1 MHz. c) Relative change of reflection and d) absolute change of refractive index of 1T-TaS$_2$ for a constant ac bias amplitude of 500 mV.
external stimuli also influence its optical properties. We observed that the optical properties of 1T-TaS$_2$ are quite sensitive to incident light intensity even at low illumination intensities of 100 mW/cm$^2$. Fig. 3.7 shows the extracted optical constants two illumination intensities, 2.5 and 250 mW/cm$^2$. A unity order change in real index is observed in this strongly correlated material.

![Figure 3.7](image)

Figure 3.7: White light intensity tunable optical properties of 1T-TaS$_2$: a) reflectance and transmittance at 2.5 and 250 mW/cm$^2$. b) corresponding electric function extracted from measurements

In order to utilize and magnify this tunability in a device, we propose a tunable metal-insulator-metal grating with intensity dependent diffraction. The schematic of the simple meta-grating is as shown in Fig 3.8a where a 20.5 nm thick 1T-TaS$_2$ layer is sandwiched between 150 nm thin silver on glass substrate and silver gratings. Finite difference time domain (FDTD) simulations show that the grating's first order diffraction peaks shift by 15.18° under low intensity and high intensity light excitation respectively (see Fig 3.8b). Further, the first diffraction intensity is enhanced by nearly 23% when illumination intensity at 516 nm wavelength increases from 2.5 to 250 mW/cm$^2$ at 5°.
Figure 3.8: Meta-blazed-grating device made by 1T-TaS$_2$ films: a) sketch of device design. From bottom to top are glass substrates, 80 nm thick Silver layer, 20 nm 1T-TaS$_2$ thin film, 5 nm Al$_2$O$_3$ protecting layer from oxygen and 1 µm Silver grating with . b) Diffraction pattern at 25 mW/cm$^2$ and 250 mW/cm white light excitation.
Chapter 4

Conclusion

Mechanically exfoliated thin films of 1T-TaS$_2$ - a quasi 2D layered material - were observed to support CDWs at room temperature. The existence of CDWs results in interesting optical and electro-optical properties. We characterized the uniaxial anisotropy in this lossy dielectric material in the visible and demonstrated in-plane electrical bias tunable optical properties. While DC bias tuned the optical properties primarily from Joule heating, ac bias tuning was an outcome of changing condensation of charge density waves. Real refractive index change in the order of 0.1 was demonstrated with both DC and ac biases. Our experiments have showed that crystalline, 1T phase of TaS$_2$ films exhibit strong photorefractive properties even at low intensities of 100 mW/cm$^2$. This tunability can lead to a modulation in the diffraction angle of a meta-blazed-grating by nearly 15.4$^\circ$ under 2.5 mW/cm$^2$ and 250 mW/cm$^2$ white light excitation, and thus making 1T-TaS$_2$ promising for imaging, displays and sensing applications.
Chapter 5

Supplemental Material

5.1 Meta-grating device

All the parameters of the meta-blazed-grating devices are listed in Fig. 5.1.

![Geometry parameters of meta-blazed-grating device simulated in Ch. 3.6](image)

Figure 5.1 : Geometry parameters of meta-blazed-grating device simulated in Ch. 3.6

Experiment demonstration of tunability of a regular meta-grating device is shown in Fig. 5.2. We detected a 1 nm diffraction peak shift at around 558 nm at 30 mW/cm² and 250 mW/cm² continuum laser excitation. The small change might be due to two reasons, the high light intensity excitation that optical properties of 1T-TaS₂ is tunable saturated, and the mismatch of thickness of 1T-TaS₂ which is sensitive by the diffraction of our device.
Figure 5.2: An experiment demonstration of tunable meta-regular-grating device: a) & b) Topography mapping by AFM and a cross section. The thickness of the 1T-TaS$_2$ is around 22 nm. c) SEM imagine of meta-grating device. The Silver grating is 150 nm wide and 80 nm heigh with 1$\mu$m grating constant. d) Normalized diffraction peak around 560 nm at 30 mW/cm$^2$ and 250 mW/cm$^2$ continuum laser excitation.
5.2 Temperature change estimation

Parameters for estimating the temperature change generated by DC bias and incident white light.

Table 5.1: Physics properties of 1T-TaS$_2$

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific heat</td>
<td>$c_p$</td>
<td>75 J·mol$^{-1}$·K$^{-1}$ [39]</td>
</tr>
<tr>
<td>Molar mass</td>
<td>$M_{mol}$</td>
<td>245.078 g/mol [40]</td>
</tr>
<tr>
<td>Mass density</td>
<td>$\rho$</td>
<td>6.86 g/cm$^3$ 3.67 × 10$^{16}$ [40]</td>
</tr>
<tr>
<td>Thickness (glass substrate)</td>
<td>$t_0$</td>
<td>150 µm</td>
</tr>
<tr>
<td>Area</td>
<td>$S$</td>
<td>7.1 × 10$^4$ µm$^2$</td>
</tr>
<tr>
<td>Current (at 0.5V DC bias)</td>
<td>$I$</td>
<td>0.9 mA</td>
</tr>
<tr>
<td>Current (at 2V DC bias)</td>
<td>$I$</td>
<td>4.8 mA</td>
</tr>
<tr>
<td>Thermal conductivity of glass</td>
<td>$\sigma_0$</td>
<td>1 W·m$^{-1}$·K$^{-1}$</td>
</tr>
<tr>
<td>White light power (average)</td>
<td>$P$</td>
<td>250 mW/cm$^2$</td>
</tr>
<tr>
<td>Absorption (average)</td>
<td>$A$</td>
<td>$\sim$50%</td>
</tr>
</tbody>
</table>

5.3 Dielectric function extraction

Only considering normal incident case. Define T-Matrix and P-Matrix as:
\begin{align*}
T_{\alpha\beta} &= \frac{1}{t_{\beta\alpha}} \begin{pmatrix} t_{\alpha\beta}t_{\beta\alpha} - r_{\beta\alpha}r_{\alpha\beta} & r_{\beta\alpha} \\ -r_{\alpha\beta} & 1 \end{pmatrix} \\
P_{\alpha}(t_{\alpha}) &= \begin{pmatrix} e^{in_{\alpha}k_{0}t_{\alpha}} & 0 \\ 0 & e^{-in_{\alpha}k_{0}t_{\alpha}} \end{pmatrix}
\end{align*}

\text{(5.1)}

where
\[ r_{\alpha\beta} = \frac{n_{\alpha} - n_{\beta}}{n_{\alpha} + n_{\beta}} \]
\[ t_{\alpha\beta} = \frac{2n_{\alpha}}{n_{\alpha} + n_{\beta}} \]

\text{(5.2)}

\( \alpha, \beta \) represents the materials, \( t_{\alpha, \beta} \) and \( n_{\alpha, \beta} \) are the thicknesses and refractive indexes of materials, respectively. \( k_{0} \) is the wavevector of light in free space. Assume ‘0’ is air, ‘1’ is 1T-TaS$_2$, ‘2’ is glass, then

\[
\begin{pmatrix} E_{t} \\ 0 \end{pmatrix} = T_{20}P_{2}(t_{2})T_{12}P_{1}(t_{1})T_{01} \begin{pmatrix} E_{0} \\ E_{r} \end{pmatrix}
\]

\text{(5.3)}

Here we assume there is no interference in the glass (set \( t_{2} = 0 \)) because we integral reflection and transmission in a narrow angle.
Bibliography


