Weak-localization effects reveal intrinsic semiconductor ground state in iodine-free TiSe₂

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Dilute impurities and growth conditions can drastically affect the transport properties of TiSe₂, especially below the charge density wave transition. In this paper, we discuss the effects of cooling rate, annealing time and annealing temperature on the transport properties of TiSe₂: slow cooling of polycrystalline TiSe₂ post-synthesis drastically increases the low temperature resistivity, which is in contrast to the metallic behavior of single-crystalline TiSe₂ due to charge doping from the residual iodine transport agent. A logarithmic increase of resistivity upon cooling and negative magnetoresistance with a sharp cusp around zero field are observed for the first time for the polycrystalline TiSe₂ samples, pointing to weak-localization effects due to low dimensionality. Annealing at low temperatures has a similar, but less drastic effect. Furthermore, rapid quenching of the polycrystalline samples from high temperatures freezes in disorder, leading to a decrease in the low temperature resistivity.

INTRODUCTION

Transition metal dichalcogenides (TMDCs) are a class of layered quasi-two dimensional materials. Owing to their low dimensionality, they span a vast area of physical properties. TiSe₂ is one such TMDC that has attracted lots of attention due to its complex electronic properties, including charge ordering [1], superconductivity with intercalation of copper or palladium [2,3], and with the application of pressure [4] or electrostatic gating [5]. On the other extreme, TiSe₂ becomes insulating with platinum doping [6], and displays potential Luttinger liquid states within domain boundaries [7] revealing the versatility of the chemical tuning of this TMDC compound.

The origin of the charge density wave (CDW) transition, occurring in TiSe₂ around 202 K [1], has been an ongoing debate for decades, with proposed mechanisms including an excitonic insulator phase [8] and the band-type Jahn-Teller effect [9]. For the former, it can arise either in a small band gap semiconductor or a semimetal [8]. Below the CDW transition, several angle-resolved photoemission spectroscopy experiments all pointed to a larger indirect gap, but whether the small normal state indirect band gap is positive or negative is still under debate [10–18]. The latter proposed CDW mechanism is independent of the free carrier concentration [19], and this cannot account for the incommensurate diffraction spots seen in TiSe₂ [1]. Recent experimental evidence favors the excitonic insulator scenario [16,19,23], but theories predict that the exciton condensation can either be a superfluid [24], or an insulator [25]. Most recently, Watson et al. presented simulations of dome-like resistivity curves centered around 150 K, simply based on a semiconducting normal state band structure with an indirect band gap, without implementing the CDW physics at all [26]. Huang et al. [27] showed insulating behavior for their polycrystalline TiSe₂ samples closest to stoichiometry, with metallicity induced by increasing Se deficiency. [27], while Cambell et al. recently revealed insulating behavior in iodine-free single crystals [28]. Historically though, single crystal samples grown by iodine vapor transport have shown metallic behavior in resistivity [1,15,29]. Bearing all of the above in mind, it is essential to reach experimental resolution of the intrinsic ground state of TiSe₂.

One problem faced in studying TiSe₂ is the inconsistency in the physical properties from sample to sample. The temperature-dependent resistivity ρ(T) shows discrepancy between single-crystalline TiSe₂ grown by I₂ vapor transport [1,15,29] and polycrystalline TiSe₂, synthesized by solid state reaction [2,18,27]. This is illustrated by the normalized ρ(T) data of TiSe₂ in Fig. 1. Even though the ρ(T) behavior is qualitatively similar between single-crystalline and polycrystalline samples with a local maximum between 100 and 200 K, at the lower temperatures ρ(T) varies drastically: metallic behavior (dρ/dT > 0) is registered in the single-crystalline sample (dashed line and open circles), explained by either a doped semiconductor picture [26] or partial gapping of the Fermi surface [1], while semiconductor-like behavior (dρ/dT < 0) is found in the polycrystalline sample (solid line). To our knowledge, no systematic study of this discrepancy exists. It is imperative to understand the intrinsic properties of TiSe₂, and the effect of the synthesis conditions on the observed resistivity measurements, before the more complex effects of chemical doping, intercalation, or pressure can be understood.

It is well known that, for TiSe₂ single crystals, the transport agent iodine might partially substitute for Se and dope the system [1,15]. Se deficiency also serves as a method of self-doping [30]. Both dopants presumably contribute additional density of states near the Fermi surface and hence enhance the conductivity on cooling. Here,
FIG. 1. A comparison of the resistivity (normalized to room temperature values) for iodine-grown TiSe$_2$ single crystals with the current $i \parallel ab$ (dashed line) or $i \parallel c$ (open circles), and polycrystalline (solid line). The full triangle is used to identify samples that are ‘As Grown, Air Quenched’ throughout the text.

we report systematic variations in the electrical transport properties of polycrystalline TiSe$_2$ without doping or Se deficiency, as a function of cooling rate, annealing time, and annealing temperature. By decreasing the rate at which samples are cooled post-synthesis, a logarithmic increase in low temperature resistivity is observed. We surmise that this increase is due to weak-localization (WL) effects in low dimensional systems. Annealing polycrystalline samples post-synthesis at low temperatures (200$\degree$C) has a similar, but less drastic effect. Our results suggest an intrinsic semiconducting ground state in TiSe$_2$, with low temperature electrical transport properties dominated by the WL effects.

METHODS

Polycrystalline samples of TiSe$_2$ were synthesized by solid state reaction with a Ti:Se ratio of 1:2.02. The excess Se was added to compensate for the partial evaporation inherent during synthesis. The samples were sealed in evacuated quartz ampoules and heated at 50$\degree$C/hr to 650$\degree$C, followed by a 48 hour dwell at this temperature. Subsequently, the samples were either cooled at different rates, or annealed at different temperatures or different times. TiSe$_2$ single crystals were grown by chemical vapor transport with I$_2$ as the transport agent. Ground elemental Ti and Se were sealed in evacuated quartz tubes with a ratio of 1:2.02 and 5 mg/cm$^3$ of iodine. The tubes were then placed in a 550$\degree$C - 650$\degree$C temperature gradient and held for 14 days, followed by controlled cooling to room temperature.

Structural characterization was done using a Bruker X-ray diffractometer with Cu k$_\alpha$ radiation. Refinements were performed using the FullProf software package [31]. The quantitative chemical composition was determined by electron probe microanalysis (EPMA) using a JEOL JXA 8530F Hyperprobe located at Rice University, Department of Earth, Environmental and Planetary Sciences, and equipped with a Schottky field emitter and five wavelength dispersive spectrometers. The analytical conditions were set to 15 kV accelerating voltage, 20 nA beam current, and beam spot size (~300 nm). The Se L$_\alpha$ and Ti K$_\alpha$ X-ray lines were simultaneously measured using counting times of 10 seconds per peak and 5 seconds per each lower and upper background, respectively. Each element was simultaneously measured on two different spectrometers in order to increase the accuracy and the statistics of the measurement. Se L$_\alpha$ was analyzed on two TAP diffracting crystals, and Ti K$_\alpha$ was analyzed on a PETL and a LiFH diffracting crystal, respectively. The standards used to calibrate the spectrometers were Se metal (Se = 99.9990 wt. %) and rutile (TiO$_2$, where Ti = 59.9400 wt. %). For quantification, the ZAF matrix correction was used. The error of analysis, determined after analyzing secondary standards is below 2%. The instrumental standard deviation (1$\sigma$) for Se and Ti in each analysis is 0.24% and 0.47%, respectively. The quantitative analyses given in element wt. % were converted to atomic ratios, and then the stoichiometry of the analyzed compound was normalized to one Ti atom.

Polycrystalline samples were pressed into pellets without sintering, and shaped into bars for resistivity measurements. DC electrical resistivity measurements were made in a Quantum Design Physical Properties Measurement System with a standard four-point probe technique for temperatures 2 - 300 K. The technique described in Ref. [32] was used for resistance measurements with current $i \parallel c$.

RESULTS AND DISCUSSION

Post synthesis cooling rate $r$

When trying to improve the quality of crystals (e.g. decrease extrinsic disorder), two commonly used techniques for metals are: (i) slow cooling to avoid quenching in disorder, and (ii) post synthesis annealing below the synthesis temperature to relieve microstrain and increase grain size [33]. In the present study, both methods were employed to minimize disorder. By contrast, quenching from high temperature was used to study the effect of enhanced disorder.

The first experiment was dedicated to testing the effect of the cooling rate post synthesis on the electrical resistivity. Three samples were synthesized as described in the
Methods. Sample A was air quenched \((r > 2000^\circ\text{C/hr})\), sample B was fast-cooled to room temperature at a rate \(r = 20^\circ\text{C/hr}\), and sample C was slow-cooled at \(r = 4^\circ\text{C/hr}\). The scaled semi-log \(\rho/\rho(300\text{ K})(T)\) plot is displayed in Fig. 2(a). While all three samples show a nearly 5 time increase in \(\rho/\rho(300\text{ K})\) on cooling to 150 K, the air-quenched sample A displays a broad local minimum centered around 60 K, while both samples B and C exhibit nearly two orders of magnitude resistivity increase down to 2 K. The large change in the resistivity as a function of cooling rate prompted the need to check sample composition for possible non-stoichiometry. The results of the EPMA analysis, displayed in Table I, indicate that all three samples are stoichiometric, with the same Ti:Se ratio of 1:2. Room temperature X-ray diffraction data (Fig. 3) does not show any measurable change in either the peak position or peak shape among the three samples, consistent with invariable lattice parameters.

When plotting \(\rho(T)\) on a semi-log scale (Fig. 2(b)), all three samples A-C show a \(-\ln T\) dependence of \(\rho(T)\) upon cooling below the CDW broad local maximum. Since no magnetic impurities are present in any of the samples, the \(-\ln T\) increase of \(\rho\) cannot be attributed to Kondo or other extrinsic magnetic effects. In TiSe\(_2\), the low dimensionality enhances two quantum corrections to the resistivity: Altshuler-Aronov corrections due to the coherent scattering of electrons by impurity-induced Friedel oscillations [34–36], and WL due to self-intersecting scattering paths [37, 38]. Upon an application of finite transverse magnetic field \(H \perp i\), the shape of the magnetoresistance MR = \([\rho(H) - \rho(0)]/\rho(0)\) is insensitive to Altshuler-Aronov corrections, while WL can be suppressed in finite magnetic fields leading to a negative MR. Fig. 2(c) shows a pronounced peak of MR centered at zero field for samples A-C, which is typical for WL effect. If we neglect contributions to the electrical transport from an inhomogeneous environment, such as grain boundaries, and interpret the data simply based on the WL theory, the MR curves are consistent with varying coherence lengths \(L_\phi\), i.e., the distance an electron goes before dephasing, with Sample A having the shortest \(L_\phi\) and Sample C having the longest \(L_\phi\) [34]. For comparison, the single crystal sample with iodine inclusions does not show WL behavior either in \(\rho(T)\) or in MR (Fig. 2(d)). EPMA reveals a 1% iodine impurity per formula unit. In our single crystal sample, the iodine inclusions might dope the system and dominate the transport property which leads to a suppression of WL behavior. A recent electrical transport study on iodine-free TiSe\(_2\) single crystals does show a large increase in electrical resistivity on cooling, qualitatively consistent with what is seen in our polycrystalline Samples B and C [28]. It will be informative to investigate the magnetic field effects on the transport properties in these iodine-free single crystals to quantitatively analyze the characteristic parameters from the WL correction. The WL effect noted here for the first time in TiSe\(_2\) had been previously reported in another TMDC, VSe\(_2\) [39]. Even though our transport data alone cannot completely rule out the possibility of the system being a semimetal, a recent simulation shows that the dome-like \(\rho(T)\) behavior around 150 K can only be replicated in a narrow band gap semiconductor framework at room temperature, but not in a semimetallic scenario [26]. Given the fact that \(d\rho/dT\)

| Cooling rate \(r\) (°C/hr) | Se  |
|----------------------------|-----|
| A: > 2000 (air quench)     | 2.02 ± 0.01 |
| B: 20                      | 2.01 ± 0.01 |
| C: 4                       | 2.00 ± 0.01 |

TABLE I. EPMA results for polycrystalline TiSe\(_2\) with variable cooling rates post synthesis corresponding to Figs. 2 and 3. Data is normalized to 1 Ti.
< 0 is observed at high temperatures (Fig. 1), we argue that TiSe$_2$ is best described as a semiconductor with a small indirect band gap. At low temperatures, impurities contribute to the carrier density and the insulating transport is dominated by WL effects. As the temperature approaches absolute zero, polycrystalline TiSe$_2$ becomes an Anderson insulator where the conduction diverges not because of a band gap, but because the localizing effects of disorder.

Cooling samples slowly after synthesis was expected to decrease the extent of disorder in the crystals and increase the average grain size. In an attempt to characterized disorder, we turn again to the X-ray refinements. There are at least four contributions to peak width in powder X-ray diffraction [33]: instrumental broadening, thermal vibrations, grain size, and microstrain. Instrumental broadening is a function of beam optics and geometry. Thermal vibrations increase the peak widths with increasing temperature. Peak width decrease as grain size increases, and increases as microstrain is increased. No variations in X-ray peak widths are measured as seen in the inset of Fig. 3 where a selection of high 2$\theta$ peaks are shown. Because all peaks are of similar width, all contributions to peak width are similar, and therefore no disorder from microstrain can be measured.

**Post synthesis annealing time t**

The next set of experiments focuses on the effect of annealing time $t$. Different pieces of sample A were annealed at $T = 200^\circ$C, for times $t$ ranging from 1 to 6 days, followed by air quenching. The low anneal temperature was chosen to relieve quenched-in disorder without adding more disorder from quenching at a high temperature. Resistivity shows a general upward trend at low temperatures on cooling for increasing $t$ (Fig. 4a). No change in stoichiometry is detected (Table II), indicating that the change in low temperature resistivity is not due to a change in the density of states near the Fermi energy from charge doping. As before, no change is recorded in the X-ray peak width and lattice parameters (not shown).

A similar study with anneal time was done on single crystals. The normalized $\rho(T)$ is plotted in Fig. 4b. Annealing did not change the low temperature transport properties when compared to the polycrystalline samples. EPMA studies looking for only Ti and Se show all similar ratios as seen in Table II. However, as stated earlier, EPMA measurements reveal iodine inclusions around 1% in single crystals for which the Ti:Se ratio is found to be 1:2. The additional density of states near the Fermi energy due to iodine accounts for the metal-like low temperature electrical transport down to 2 K in single crystalline TiSe$_2$.

**Post synthesis annealing temperature T**

The next experiment aims to purposefully induce disorder into the TiSe$_2$ by quenching, followed by annealing at different temperatures $T$. Different single crystal pieces were annealed for 2 days at different temperatures $T$ between 200 and 1200$^\circ$C. After annealing, all samples were quenched. Normalized $\rho(T)$ data is plotted in Fig. 5.

For anneal temperatures $T$ below the growth temperature $T_{\text{growth}} = 650^\circ$C (triangles, Fig. 5a), the low
FIG. 4. (a) Comparison of polycrystalline $\rho/\rho(300 \text{ K})$ for TiSe$_2$ samples annealed at 200°C in one day increments up to six days. With increase in anneal time, the low temperature resistivity increases. (b) The same comparison for TiSe$_2$ single crystals. The low temperature resistivity is dominated by iodine impurities.

Temperature resistivity of the polycrystalline samples increases compared to that of the as-grown sample, much the same as the result shown in Fig. 4(a). For anneal temperatures at (square) or above (star) the synthesis temperature, the low temperature resistivity decreases. However, below 20 K the resistivity increases on cooling for all annealing temperatures $T$. Our EPMA data shows no systematic loss of selenium with increased anneal temperature (Table III), whereas X-ray diffraction patterns (Fig. 6) indicate significant peak broadening for samples quenched from 1200°C (star) indicating microstrain caused by quenching at such a high temperature. Though there are small variations in lattice parameters, the variations are less than 0.1% of the as grown (upwards triangle), so the change in resistivity is not due to a change in the unit cell.

For comparison, analogous data is shown in Fig. 5(b) for TiSe$_2$ single crystals. Besides the differences in low temperature resistivity, which can be explained by iodine impurities, the normalized $\rho(T)$ shows qualitatively similar features as the polycrystalline samples. The trend of decreasing peak height below the CDW transition is qualitatively similar to that previously attributed to non-stoichiometry [1] . Though a Se deficiency is seen in the sample annealed at 1200°C, the polycrystalline counterpart suggests that the decrease in the anomaly height is not due to doping, but rather an increase in quenched disorder. Remarkably, the 1200°C single crystal (star, Fig. 5(b)) shows metallic behavior for the whole temperature range, and no anomaly in $\rho(T)$. Consistent with the observations of the most substantive structural changes at this temperature (Fig. 6), this signals that self doping, disorder, grain boundary freezing, or more, inhibit the intrinsic properties of TiSe$_2$ at excessively high annealing temperatures.
A seeming consensus concerning electrical transport studies is that single crystal data is often more reliable than polycrystalline samples, because the data the latter can be plagued by grain boundary effects and lack of anisotropy details. We confirm that the electrical transport in TiSe$_2$ single crystals is nearly isotropic (Fig. 1), consistent with previous reports. This rules out anisotropy as the cause of differences in transport between polycrystalline and single crystalline samples.

Furthermore, we expect that the overall behavior of polycrystalline samples and single crystals to be similar, since the grain boundaries should contribute only an additive temperature-independent term to the bare Drude conductivity. Our study indicates that TiSe$_2$ behaves like a small gap semiconductor where the electrical transport is largely localized by residual impurities towards zero temperature. In addition, the drastic decrease in the CDW anomaly upon annealing is also consistent with disorder (Fig. 5). Hildebrand et al. reported a decrease in CDW domains with increasing disorder. As the CDW domain size becomes smaller than the bulk exciton Bohr radius, the holes and electrons break into individual charge carriers, reducing the magnitude of the CDW anomaly. Though no systematic differences of disorder were measurable in our work, the trend in resistivity is consistent with a decrease in disorder for a decrease in cooling rate and an increase in annealing time, and both of which are expected in resulting better crystallization. Also, because no measured selenium deficiency is found in powdered samples, the disorder is a different effect than doping reported by Huang et al.

**CONCLUSIONS**

We have systematically studied the effects of the cooling rate, and temperature and time dependence of post-synthesis annealing on the observed electrical transport properties of TiSe$_2$. For the first time, the weak-localization effect is found in polycrystalline TiSe$_2$ samples, embodying the quantum corrections to the electrical transport properties in low dimensional systems. At low temperatures results on polycrystalline TiSe$_2$ are consistent with a semiconducting-like ground state with low temperature-independent term to the bare Drude conductivity. Our study indicates that TiSe$_2$ behaves like a small gap semiconductor where the electrical transport is largely localized by residual impurities towards zero temperature. In addition, the drastic decrease in the CDW anomaly upon annealing is also consistent with disorder (Fig. 5). Hildebrand et al. reported a decrease in CDW domains with increasing disorder. As the CDW domain size becomes smaller than the bulk exciton Bohr radius, the holes and electrons break into individual charge carriers, reducing the magnitude of the CDW anomaly. Though no systematic differences of disorder were measurable in our work, the trend in resistivity is consistent with a decrease in disorder for a decrease in cooling rate and an increase in annealing time, and both of which are expected in resulting better crystallization. Also, because no measured selenium deficiency is found in powdered samples, the disorder is a different effect than doping reported by Huang et al.

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