Photon-Induced Selenium Vacancies in TiSe₂

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TiSe₂ is a member of transition metal dichalcogenide family of layered van-der-Waals materials that exhibits some distinctive electronic and optical properties. Here, we perform Raman spectroscopy studies on single crystal TiSe₂ to investigate photon-induced defects associated with formation of selenium vacancies. Two additional E_g phonon peaks are observed in the laser-irradiated regions, consistent with Raman spectra of selenium deficient TiSe₂. Temperature dependent studies of the threshold laser intensity necessary to form selenium vacancies show that there is a linear dependence. We extract the relevant activation energy for selenium vacancy nucleation. The impact of these results on the properties of strongly correlated electron states in TiSe₂ are discussed.

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Transition metal dichalcogenides (TMDs) exhibit series of unique electronic properties ranging from charge density wave (CDW) order to superconductivity. 1T-TiSe₂ is a quasi-2D layered material with a trigonal symmetry that has been studied for over 30 years³–⁹. Only recently it was discovered that the CDW in this material has excitonic origin⁵,⁶ and a chiral order,¹⁰,¹¹ which might have implications on fundamental understanding of the strongly correlated electron systems. On the other hand, the ability to separate charges in materials with reduced dimensionality is of great interest for many potential applications.⁷,⁸ Due to its specific structural and electronic properties TiSe₂ has also been considered as alternative to graphene electronics,¹²,¹³ in thermoelectric applications¹⁴,¹⁵ and as a cathode material in batteries.¹⁶

The strongly correlated electron behavior in TMDs is usually attributed to their quasi-two-dimensional structure consisting of X-M-X layers (M—transition metal and X—chalcogen) weakly bound together by van der Waals forces.¹⁶ Further interest in these systems has been stimulated by the changes in their bulk electronic properties upon reduction to a single monolayer. The modification of the electronic properties in 2D layered systems is due to the changes in the electronic and phonon band structure when the systems are reduced to a single X-M-X layer.¹⁷,¹⁸ Fabrication of single or few layer TMDs proceeds either by exfoliation from single crystals¹,¹³,¹⁹ or through chemical growth of thin films.²⁰–²² The first method has been favored by many researchers ever since it was first used with graphene, as it tends to yield better crystalline quality and, therefore, is very suitable for studying the fundamental physical properties. However, exfoliation is not scalable, making it ill-suited for device fabrication and integration with other thin film materials and processes.

On the other hand, physical and chemical vapor deposition methods are very flexible in terms of control of thickness and chemical composition of the dichalcogenide layers. Up to now TiSe₂ monolayers have proven difficult to obtain through methods other than molecular beam epitaxy.²² Synthesized thin film TMDs often suffer from high concentration of defects and lack of long range crystalline order.¹⁶ In TiSe₂ the most frequent defects are selenium vacancies¹,²³. The concentration of selenium vacancies depends strongly on the conditions of film growth, especially growth temperature, similar as in the case of single crystal growth¹,². Selenium deficiencies are often detrimental to the charge density wave order¹⁶ as their presence changes the nature of the material from semiconducting to semimetallic. Therefore, the characterization of the defects and their dynamics is of utmost importance.

Raman spectroscopy is one of the main tools utilized to study layered TMDs, as the symmetric A₁g breathing phonon mode and E_g layer shearing mode are sensitive to inter- and intra-layer properties of the structure.²⁴ As in the case of graphene, Raman spectra can distinguish between single and few layers of TMD on the surface. Indeed, both resonant and non-resonant Raman spectroscopy has already been used to distinguish multilayered thin films of MoS₂,²⁵ WS₂,²⁶ MoTe₂,³ and other members of the TMD family.⁴ In the present work we study the evolution of selenium vacancies in high quality TiSe₂ single crystals as they appear in Raman spectra through Raman laser induced vaporization of the selenium atoms. The temperature dependent studies allow us to estimate the activation energy for selenium vacancy nucleation, an important parameter if considering TiSe₂ as material for electronic and optical applications.

High quality single crystals of TiSe₂ were grown using chemical vapor transport method¹,²,²⁷ and characterized using EDS, XRD and variable temperature electrical transport. One of the signatures of low level of
intrinsic defects in the single crystals is the high charge density peak in resistivity at the CDW transition (2.5–3.5 times the room temperature resistivity) and low level of defect concentration as observed by scanning tunneling microscopy. Variable temperature Raman spectroscopy measurements were conducted at the Center for Nanoscale Materials at Argonne National Laboratory using a Renishaw InVia Raman microscope with a 514 nm argon ion laser source and a ∼1.5 μm diameter spot size. The spectrometer is equipped with variable temperature cell capable of operating between 80–400 K. All the experiments were conducted in the presence of ultra-high pure nitrogen exchange gas at normal pressure. Fig. 1a shows Raman spectra on freshly cleaved surface of TiSe$_2$ single crystal. At room temperature one can see the normal phase shearing mode $E_g$ and breathing mode $A_{1g}$ peaks. As the temperature is lowered below the CDW transition of ∼200 K we see the emergence of additional peaks that reflect the change in lattice symmetry. The CDW doubles the period of the crystal lattice to $2a_0 \times 2a_0 \times 2c$ and induces additional Raman peaks: the 315 cm$^{-1}$ peak is first seen below ∼160 K, in agreement with previous measurements. The charge density wave $A_{1g}$ peak at 110 cm$^{-1}$ becomes fully observable only at temperatures lower than ∼100 K.

Uniform heating of the TiSe$_2$ single crystal above room temperature makes the crystal structure more susceptible to laser induced change. Fig. 2 shows the evolution of Raman spectra of the TiSe$_2$ single crystal from room temperature and up to 400 K. At 300 K one notices a broad Raman background signal centered at around 250 cm$^{-1}$. There are also enhanced fluctuations of the background intensity in the spectrum around this frequency. As the temperature is increased, the broad background slowly evolves into a set of distinct peaks. At 360 K we observe a broad increase in the background at near 250 cm$^{-1}$. This broad peak is consistent with previous Raman experiments performed on non-stoichiometric TiSe$_{2-x}$ with high concentration of selenium vacancies. As the temperature is raised further, the broad background evolves into distinct peaks that are made up of two Raman modes centered at 241 and 263 cm$^{-1}$. They are shown in the inset of Fig. 2 and were obtained by reducing the laser power from 1.87 mW to 1.05 mW and moving the laser spot outside the perimeter of the original beam profile. The result indicates that high beam powers damage the sample surface within the laser beam profile, and within a much larger radius (∼100 μm depending on the excitation power) some of the surface selenium atoms sublime leaving selenium vacancies on the TiSe$_2$ single crystal surface.

To understand the relevant temperatures and activation energies for nucleation of selenium vacancies we
conducted systematic experiments by varying both laser beam power and temperature. Each measurement was made on large atomically flat planes of the single crystal surface with no edges in the microscope image. Raman spectrum at each temperature was taken for 3 min before blocking the laser beam and moving on to the next higher temperature setpoint. Each spectrum was taken on a different and pristine location on the surface of the single crystal in order to avoid effects from previous laser irradiation. In Fig. 3 Raman intensity at 253 cm$^{-1}$ is plotted versus temperature for multiple beam powers, each showing different onset of the peak increase with temperature. The threshold temperature beyond which the peak height at 253 cm$^{-1}$ starts increasing marks the onset of irreversible damage done to the crystal surface. The inset in Fig. 3 shows a linear relationship between the beam power and threshold temperature $T_c$ for irreversible damage, suggesting that thermal effects are responsible for selenium vaporization. The extrapolation of the curve to vanishing laser power leads to zero crossing at 435 K. This suggest of a relatively low temperature threshold at which the process of generation of selenium vacancies starts taking place. Since this process is thermally activated, we fit the peak height vs normalized temperature with Arrhenius dependence and find that the activation energy for selenium vacancy generation is $0.52 \pm 0.07$ eV. Our results of laser damage of TiSe$_2$ single crystals very much resemble the experiments on CdZnTe in which the processes of evaporation of cadmium and migration of tellurium to the damaged sites takes place due to the laser-surface interaction.

The inset in Fig. 3 shows a linear relationship between the beam power and threshold temperature $T_c$ for irreversible damage, suggesting that thermal effects are responsible for selenium vaporization. The extrapolation of the curve to vanishing laser power leads to zero crossing at 435 K. This suggest of a relatively low temperature threshold at which the process of generation of selenium vacancies starts taking place. Since this process is thermally activated, we fit the peak height vs normalized temperature with Arrhenius dependence and find that the activation energy for selenium vacancy generation is $0.52 \pm 0.07$ eV. Our results of laser damage of TiSe$_2$ single crystals very much resemble the experiments on CdZnTe in which the processes of evaporation of cadmium and migration of tellurium to the damaged sites takes place due to the laser-surface interaction. The results on the photon induced nucleation of selenium vacancies in TiSe$_2$ have broader implications for both fundamental studies of TiSe$_2$ as well as potential practical applications. The interest in TiSe$_2$ dichalcogenide has been due to its excitonic nature of charge density wave state, superconductivity in Cu$_x$TiSe$_2$ and $\text{Pd}_x\text{TiSe}_2$, as well as due to unique observation of the chiral charge density waves. Fundamental studies of these correlated states and their coexistence have been on the rise recently, as the dichalcogenide system is structurally relatively simple and can provide some answers in regards to the mechanisms of correlated electron states in other classes of materials like perovskite high temperature superconductors or pnictides. Since TiSe$_2$ is a compensated semimetal with very large Hall coefficient at low temperatures, the correlated electron states are very susceptible to the level of intrinsic doping. Therefore, any fundamental studies should take into account the selenium vacancy concentration levels and the relatively low activation energy for their nucleation. The concentration and dynamics of selenium vacancies could be very important in TiSe$_2$ thin films as the Raman peaks associated with these defects are strong in synthesized films. With reduced dimensionality of the system (from 3D crystals to 2D thin films), the activation energy for selenium vacancy formation could further decrease and make the 2D system metastable even at room temperatures. The intrinsic doping due to vacancies might suppress the charge density wave correlations and reduce the signature of charge density wave phase normally observed resistivity vs temperature measurements. A possible method to prevent selenium vaporization and at the same time enhance the CDW transition temperature in 2D TiSe$_2$ could be the encapsulation using hexagonal boron nitride, as shown recently. Clearly, more work needs to be done in this area to understand the dynamics of selenium in TiSe$_2$ and with recent advances in tip-enhanced Raman spectroscopy one could possibly obtain sufficient spatial and spectroscopic resolution.

Raman spectroscopy studies on single crystal TiSe$_2$ show a photon-induced defect signature associated with nucleation of selenium vacancies. Two additional $E_g$ phonon peaks at 241 and 263 cm$^{-1}$ are observed in the laser irradiated regions, consistent with Raman spectra of selenium deficient TiSe$_2$. Temperature dependent studies of the threshold laser intensity necessary to form selenium vacancies show that there is a linear dependence, suggesting thermally activated character of the process. The extrapolation of the onset temperature of the photon-induced damage shows that the process of selenium vacancy nucleation could start at temperatures as low as 435 K without the assistance of any photon sources.
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1F. J. Di Salvo, D. E. Moncton, and J. V. Waszczak, Phys. Rev. B 14, 4321 (1976).
2J. A. Wilson, Phys. Status Solidi B 86, 11 (1978).
3H. Guo, T. Yang, M. Yamamoto, L. Zhou, R. Ishikawa, K. Ueno, K. Tsukagoshi, Z. Zhang, M. S. Dresselhaus, and R. Saito, Phys. Rev. B 91, 205415 (2015).
4E. Lorchat, G. Froehlicher, and S. Berciaud, ACS Nano 10, 2752 (2016).
5H. Cercellier, C. Monney, F. Clerc, C. Battaglia, L. Despont, M. G. Garnier, H. Beck, P. Aebi, L. Patthey, H. Berger, and L. Forro, Phys. Rev. Lett. 99, 146403 (2007).
6C. Monney, E. F. Schwier, M. G. Garnier, N. Mariotti, C. Didiot, H. Cercellier, J. Marcus, H. Berger, A. N. Tittov, H. Beck, and P. Aebi, New J. Phys. 12, 125019 (2010).
7M. M. Fogler, L. V. Butov, and K. S. Novoselov, Nature Commun. 5, 4555 (2014).
8T. Korn, S. Heydrich, M. Hirner, J. Schmutzler, and C. Schueller, Appl. Phys. Lett. 99, 102109 (2011).
9R. Bhattachary, A. Singh, D. K. Aswal, S. K. Gupta, G. S. Okram, V. Ganasean, D. Venkateshwarl, C. Surgers, M. Navaneethan, and Y. Hayakawa, Appl. Phys. A-Materials Science and Processing 111, 465 (2013).
10I. Ishioka, Y. H. Liu, K. Shimatake, T. Kurosawa, K. Ichimura, Y. Toda, M. Oda, and S. Tanda, Phys. Rev. Lett. 105, 176401 (2010).
11J.-P. Castellan, S. Rosenkrantz, R. Osborn, Q. Li, K. E. Gray, X. Luo, U. Welp, G. Karapetrov, J. P. C. Ruff, and J. van Wezel, Phys. Rev. Lett. 110, 196404 (2013).
12P. Chen, Y. H. Chan, X. Y. Fang, Y. Zhang, M. Y. Chou, S. K. Mo, Z. Hussain, A. V. Fedorov, and T. C. Chiang, Nature Commun. 6, 8943 (2015).
13L. J. Li, E. C. T. O’Farrell, K. P. Loh, G. Eda, B. Ozyilmaz, and A. H. C. Neto, Nature 529, 185 (2016).
14R. Bhattachary, A. Basu, S. Ahmad, A. K. Chauhan, G. S. Okram, P. Bhatt, M. Roy, M. Navaneethan, Y. Hayawka, A. K. Debath, A. Singh, D. K. Aswal, and S. K. Gupta, ACS Appl. Mater. Interfaces 6, 18619 (2014).
15Y. Gu, Y. Katsura, T. Yoshino, H. Takagi, and K. Taniguchi, Sci. Rep. 5, 12486 (2015).
16R. Lv, J. A. Robinson, R. E. Schaan, D. Sun, Y. Sun, T. E. Mallouk, and M. Terrones, Acc. Chem. Res. 48, 56 (2015).
17Y. Zhu, Y. C. Cheng, and U. Schwingenschlogl, Phys. Rev. B 84, 153402 (2011).
18S. Lebegue and O. Eriksson, Phys. Rev. B 79, 115409 (2009).
19A. Ubaldini and E. Giannini, J. Cryst. Growth 401, 878 (2014).
20J.-P. Peng, J.-Q. Guan, H.-M. Zhang, C.-L. Song, L. Wang, K. He, Q.-K. Xue, and X.-C. Ma, Phys. Rev. B 91, 121113(R) (2015).
21N. D. Boscher, C. J. Carmalt, and I. P. Parkin, Chem. Vap. Deposition 12, 54 (2006).
22K. Sugawara, Y. Nakata, R. Shimizu, P. Han, T. Hitosugi, T. Sato, and T. Takahashi, ACS Nano 10, 1341 (2016).
23B. Hildebrand, C. Didiot, A. M. Novello, G. Monney, A. Scarfato, A. Ubaldini, H. Berger, D. R. Bowler, C. Renner, and P. Aebi, Phys. Rev. Lett. 112, 197001 (2014).
24W. Zhao, P. H. Tan, J. Liu, and A. C. Ferrari, J. Am. Chem. Soc. 133, 5941 (2011).
25P. Soubelet, A. E. Bruchhausen, A. Fainstein, K. Nogajewski, and C. Faugeras, Phys. Rev. B 93, 155407 (2016).
26M. Staiger, R. Gillen, N. Scheuschner, O. Ochedowski, F. Kampmann, M. Schleberger, C. Thomsen, and J. Maultzsch, Phys. Rev. B 91, 195419 (2015).
27C. S. Oglesby, E. Bucher, C. Kloc, and H. Hohl, J. Cryst. Growth 137, 289 (1994).
28M. Iavarone, R. Di Capua, X. Zhang, M. Golalikhani, S. A. Moore, and G. Karapetrov, Phys. Rev. B 85, 155103 (2012).
29C. S. Snow, J. F. Karpus, S. L. Cooper, T. E. Kidd, and T. C. Chiang, Phys. Rev. Lett. 91, 136402 (2003).
30S. Sugai, K. Murase, S. Uchida, and S. Tanaka, Solid State Commun. 35, 433 (1980).
31J. A. Holy, K. C. Woo, M. V. Klein, and F. C. Brown, Phys. Rev. B 16, 3628 (1977).
32H. Barath, M. Kim, J. F. Karpus, S. L. Cooper, P. Abbamonte, E. Fradkin, and R. J. Cava, Phys. Rev. Lett. 100, 164602 (2008).
33A. Hawkins, E. Villa-Aleman, M. C. Duff, D. B. Hunter, A. Burger, M. Groza, V. Buliga, and D. R. Black, J. Electron. Mater. 37, 1438 (2008).
34L. C. Snow, A. Hawkins, M. C. Duff, M. Groza, V. Buliga, and A. Burger, J. Electron. Mater. 38, 1522 (2009).
35E. Morosan, H. W. Zandbergen, B. S. Dennis, J. W. G. Bos, Y. Onose, T. Klimczuk, A. P. Ramirez, N. P. Ong, and R. J. Cava, Nature Phys. 2, 544 (2006).
36E. Morosan, K. E. Wagner, L. N. Zhao, Y. Hor, A. J. Williams, J. Tao, Y. Zhu, and R. J. Cava, Phys. Rev. B 81, 094524 (2010).
37A. M. Novello, B. Hildebrand, A. Scarfato, C. Didiot, G. Monney, A. Ubaldini, H. Berger, D. R. Bowler, P. Aebi, and C. Renner, Phys. Rev. B 92, 081101(R) (2015).
38P. Goli, J. Khan, D. Wickramaratne, R. K. Lake, and A. A. Balandin, Nano Lett. 12, 5941 (2012).
39J. Li, W. J. Zhao, B. Liu, T. H. Ren, G. Eda, and K. P. Loh, Appl. Phys. Lett. 109, 141902 (2016), 10.1063/1.4963885.
40N. Jiang, D. Kurouski, E. A. Pozzi, N. Chiang, M. C. Hersam, and R. P. V. Duyne, Chem. Phys. Lett. 659, 16 (2016).