Multiple exciton generation and giant external quantum efficiency in VO₂

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(Dated: February 11, 2022)

Multiple exciton generation (MEG) is a widely studied phenomenon in semiconductor nanocrystals and quantum dots wherein photo-excited carriers relax by generating additional electron-hole pairs. Here, we present the first experimental observation of MEG and the same leading to giant external quantum efficiency (EQE) in VO₂, a prototype strongly correlated material. By employing a photo-excitation (λ ~ 488 nm) of ~ 4.2 times the bandgap, EQE in VO₂ is enhanced up to ~ 170 % at room temperature. Temperature dependent experiments exhibit the direct relation between MEG and strength of electron correlation and suggest that such a phenomenon could be exploited in large number of strongly correlated materials for high performance solar cell research in near future.

Keywords: strongly correlated material, VO₂, multiple excition generation, external quantum efficiency, Photo-conductivity, Insulator to metal transition

VO₂ is one of the widely studied strongly correlated electron material and famous for its near room temperature reversible first-order insulator to metal transition (IMT). It enters from low temperature insulating monoclinic (P2₁/c) state into high temperature metallic rutile (P4₂/mmm) state at ~ 68°C. IMT of VO₂ is one of the most intriguing phenomenon because both, the structure and the electron correlation, contribute to it. Insulating phase of VO₂ absorbs light from visible to infra-red (IR) range due to its unique band structure and shows an optical band gap of ~ 0.6 eV corresponding to the gap between the α₁g (V 3dα) and the ε₂g bands. A large number of experimental and theoretical investigations on the VO₂ have shown importance of the strong electron correlation.[10][14][16] i.e. band gap in VO₂ is a result of the strong Coulomb interaction between the Vanadium 3d electrons.[1][2][4]

Materials with strong electron correlation may exhibit fascinating and important photo-induced effects such as multiple exciton generation (MEG) or carrier multiplication (CM) where absorption of single photon having energy above the threshold energy (E₉) excites multiple electrons from the valence band to conduction band. MEG has the potential to significantly enhance the solar cell efficiency which may lead to the realization of next generation solar cells.[13][20] Threshold energy required for the MEG process is hν₉ = (2 + m_e/m_h)E_g.[23] In a strongly correlated insulator (SCI) the localized electron form an electronic system in which the residual effective electron-electron interaction can lead to faster decay of initially photo-excited electron-hole pair into multiple electron-hole pairs through the process called impact ionization (II) and can result into effective MEG. The proposed mechanisms for MEG in different materials like quantum dots, semiconductor nanocrystals and halide perovskites, strongly correlated material are different.[10][13][20][22][24]

For narrow-gap Mott insulators Manousakis et al.[13] theoretically studied the photovoltaic effect and found that the quantum efficiency in an appropriate narrow-gap Mott insulator can be significantly enhanced due to II caused by the photo-excited ‘hot’ electron-hole pairs. By ab-initio methods, Coulter et al.[14] estimated that the II rate in strongly correlated insulator is approx two orders of magnitude higher than in the Si and much higher than rate of hot electron-hole decay arising due to e-phonon relaxation.[14] Werner et al.[15] calculated role of II in the thermalization of photo excited Mott insulators and emphasized that if the Mott gap is smaller than width of the Hubbard bands the kinetic energy of individual carriers can be large enough to produce additional multiple carriers via a process analogous to II. [13] In case of halide perovskites it has been shown that the generated multiple carriers by means of II acquire lighter mass and this could allow their efficient separation before recombination.[25] In conventional semiconductors typical time scale for II (1-100 ps) is much larger than the time scale of electron-phonon scattering (0.1-1 ps) therefore EQE value does not cross the Schokley-Queisser (SQ) efficiency limit[26] while in SCIs typical time scale for II rate is of the order of few fs, therefore EQE may enhance significantly (see Fig[1]) and can overcome the SQ limit.

Here, we have experimentally studied the temperature dependence of MEG and EQE in VO₂. In order to achieve sufficient impact ionization photon energy must be sufficiently higher than E₉, as is reported in the cases of quantum dots, semiconductor nanocrystals and halide perovskites et al.[10][13][20][22][24] We have utilized photons of ~ 2.54 eV (6.25*E_g). A novel phase sensitive ac photo-conductivity measurement has been utilized to distinguish the photo-thermal and II driven carrier generations. The EQE have been quantified at various temperatures from 220 K (highly electron correlation rich state) to 350 K (when VO₂ is starting to be metallic, T₉IMT ~ 334 K (Fig[1][b])) and at room temperature EQE is found to increase giantly, up to ~ 170%.

The VO₂ thin film used in this study is grown on Si [100] substrate using pulsed laser deposition technique. A KrF excimer laser, λ = 248 nm, repetition rate of 5Hz and pulse energy of 370 mJ, was focused onto the V₂O₅ target with a fluence of ~ 1.1 J/cm². During deposi-
FIG. 1: Cartoon showing the origin of enhanced external quantum efficiency in strongly correlated material via faster impact ionization process. a) In conventional semiconductor, typical time scale for electron-phonon relaxation is less, therefore electron-phonon relaxation rate is much faster than the impact ionization rate. b) opposite is true for strongly correlated insulator.

tion ultrasonically cleaned Si substrate was maintained at a temperature of \( \approx 670^\circ\text{C} \). Deposition was performed for about 40 minutes in an oxygen partial pressure of \( \approx 8 \text{ mTorr} \). Bruker D8 X-ray diffractometer with Cu K\( \alpha \) radiation was utilized to confirm the VO\(_2\) phase. Temperature dependent four probe resistivity measurements were performed to confirm the insulator to metal transition in grown VO\(_2\) thin film by using a home developed setup which utilizes a Cryocon 22C temperature controller, Keithley 2401 source meter and Keithley 2182A nanovoltmeter. Raman spectra was collected in back-scattering geometry using a 10 mW Ar (473 nm) laser as an excitation source coupled with a LABRAM-HR micro-Raman spectrometer equipped with a 50X objective. For photo-conductivity measurements an Ar ion gas laser (488 nm) was used. DC photo-conductivity measurement has been performed using the Keithley 6517B electrometer. SR 860 Lock-in Amplifier and optical chopper (maximum operating frequency 3.9 kHz) were employed for phase sensitive ac photo-conductivity measurements. Temperature coefficients of resistance in insulating and metallic phases are significantly different, so any temperature rise due to laser illumination may have diverse contribution in the observation of photo currents in the two phases. Therefore, during photo current measurements we have kept the laser power to a very low value \( \sim 0.33\text{W/cm}^2 \). During the photo-conductivity experiment, temperature was controlled with the help of Lakeshore 335 temperature controller in closed cycle refrigerator (advanced research system), where VO\(_2\) film is mounted on the cold head and can be accessed via optical transparent quartz window fitted on the vacuum shroud of CCR. Maximum temperature in our experiments was limited to 350 K (maximum operating temperature of the CCR).

In VO\(_2\) photo-thermal and II driven carrier generation can be distinguished in frequency dependent measurement\(^{22}\) as MEG dominates at higher frequencies. Moreover, II driven carriers will be faster and may differ in phase from photo-thermal driven carriers. The in-phase component of ac photo-conductivity of the correlated electron rich insulating phase (220 K) and of the metallic phase (350 K) having lack of correlated electron is shown in Fig.2(a) and 2(b), respectively. At 220 K, it is observed that at lower frequencies \( \leq 3 \text{ kHz} \) the photo-excited carriers which are actually participating in photocurrent (negative values) have hole like response (higher effective mass). At higher frequencies \( > 3 \text{ kHz} \) the photo current values become positive indicating typical electron.

FIG. 2: Frequency and temperature dependence of the in-phase and out-of-phase component of the photo-current and EQE obtained from total photo-current. Frequency dependent photo-current a) in insulating state at 220 K b) in metallic state at 350 K. c) Bias voltage and frequency dependence of EQE at 300 K which is showing that the maximum EQE value is achieved at highest frequency which is purely MEG driven due to correlated electrons. d) Behaviors of in-phase component, \( I_x \) (solid symbol), and out-of-phase component of photo-current, \( I_y \) (hollow symbol), with varying frequency at different temperatures (0 - 10 V bias).
like response (lesser effective mass). Above observation is found to be consistent when bias voltage sign is reversed. At 350 K, insulating phase may still be present although little, therefore finite current is observed at low bias voltages. Similar behavior were observed also in dc measurements (Fig. S3(b)).

At higher frequencies > 3 kHz, impact ionization process is dominating. From ac photo-current measurements we have calculated the external quantum efficiency (EQE). Bias voltage and frequency dependent EQE at 300 K is plotted in Fig. 2(c). EQE is related to the material’s sensitivity to the light and determines the number of photo-induced carriers per incident photons, as detailed in supplementary. The carriers generated due to involvement of Coulomb interaction energy will decay much faster and will also recombine faster because of their high velocity near the Fermi level ($E_F$), however, high dielectric constant of VO$_2$ ($\epsilon \approx 100$) would enable the large separation between the photo excited electron-hole pairs within very short time scale. Applied bias voltage further helps in pulling the generated carriers before their recombination. At 300 K, EQE value is observed to be maximum at 3.9 kHz ($@ -10$ V) and at these frequencies photo-current is mainly due to photo-induced MEG. By comparing the EQE values at low frequencies and at high frequencies, we find that photo-current due to MEG is larger at higher frequencies.

The observations of individual components of photo-current, in-phase (Ix) and out-of-phase (Iy), with varying frequencies becomes interesting because both the components have different behavior with frequencies. Fig. 2(d) show the frequency response of the both, in-phase as well as out-of-phase components of photo-current at different temperatures in the insulating as well as metallic phase. It is clearly seen that at temperatures 220 K and 250 K, when the VO$_2$ is strongly insulating, both the components of photo-current decreases with increasing frequency, however, at 270 K and beyond ($< T_{IMT}$) when VO$_2$ has weaker electron correlation strength starts to resemble photo-induced metallicity. It is observed that Iy first changes its sign from positive to negative and becomes more negative with increasing frequency and Ix component becomes less negative with increasing frequency. These are the prototypical signatures of carrier multiplication. This is supported also by switching behavior of $\theta$ (phase shift) with varying frequency for before and after switching into the metallic phase (see inset (ii) of Fig. 3(a)). The photo-induced IMT is ascertained by jump in $\theta$ values from large negative to less negative (at 1 and 2 kHz) and to positive values (at 3 and 3.9 kHz) with simultaneous jump in photo-current. Complete detail of temperature dependent behavior of in-phase (Ix), out-of-phase (Iy), total current (Ip) and $\theta$ at different temperatures with varying frequencies can be seen in Fig. S4, S5, S6 and S7, respectively. Our temperature and frequency dependent observations of Ix and Iy components of total photo-current demonstrates the direct sensitivity to temperature dependent behavior of the electron correlation. These results show that VO$_2$ although remains insulator (below IMT temperature) but band gap (i.e. the electron correlation strength) decreases by increasing the temperature and this is consistent with the earlier reported results of temperature dependent photo-electron spectroscopy and infrared absorption measurements.
in insulating phase of VO₂. In VO₂ with increasing temperature due to rise in apical V-O bond lengths the Oxygen 2p and V 3d (p-d) hybridization (responsible for optical band gap) weakens and leads to falling of the eᵦ band near the Fermi energy which results into decrement of band gap as well as correlation energy (Fig. S1(c)).

By the above analogy with increasing the temperature, from 220 K to 250 K, threshold energy requirement for MEG would be lesser. Therefore, at higher temperatures, due to the presence of weakened insulating phase, multiple carrier generation will consequently increase and VO₂ can easily acquire critical carrier density for metal like behavior already at a lower temperature (than actual IMT). In the in-phase component of photocurrent (Fig.3(a)) with varying frequency an abrupt jump in the photo-current indicates a photo-induced insulator to metal transition. At this temperature (250 K) reduced threshold energy has enabled much larger MEG. This can be explained in the context of critical carrier density driven insulator to metal transition (Mott criterion) allows critical carrier density driven insulator to metal transition in VO₂. At a given temperature, bias voltage required to observe the jump in photo-current is same at all frequencies (Fig. 3(a)). This directly indicates that one just requires to overcome the correlation energy at that temperature. However, the transition magnitude is higher at lower frequencies (inset (i) of Fig.3(a)). This is because the photo-conductivity at low frequencies is mainly contributed by hole like carriers. It is to be noted that jump in photo-current (photo-induced IMT) is followed by a hysteresis also, which is a typical signature of first order phase transition. The bias voltage required to observe the jump in photo-current is found to reduce with temperature (Fig. S8(a)). To compare the pure MEG driven quantum efficiency of the system we have calculated the EQE at different temperatures for 3.9 kHz (shown in Fig. 3(b)) at -10 V bias. One can clearly see that in insulating phase, with increasing temperature EQE increases but when the VO₂ enters into metallic state the EQE diminishes due to lack of correlated electrons. Lower EQE in highly insulating state (220 K) is because photon energy is not sufficient enough to break the correlation at that temperature.

In case of strongly correlated electron material, for MEG the incident photon of energy should be several times higher than the Mott band gap so that several electron hole pairs can be created. II process is only expected for interactions U ≤ 4 |p|. For larger U values, the energy associated with scattering between states within the bandwidth is not enough to excite electrons across the gap which is consistent with our temperature dependent results. In a room temperature pump-probe optical spectroscopy study on VO₂, Holleman et al. studied the role of II and found the signatures of CM. Our results exhibit a large dependence of the photo current on frequency and bias voltage in insulating phase but not in metallic phase. In insulating phase, by varying the optical chopping frequency sign conversion of photo-current has been observed which indicates the role of effective masses of photo-excited carrier. At lower frequencies (< 3 kHz) all those electrons will participate in photo excitation which are at a₁g band (having higher effective mass). Therefore, photo-current shows the hole like behavior (for positive bias voltage negative photo-current and for negative bias positive photo-current Fig.3(a) and Fig. S4(a,b,c)). With increasing frequency photo-current becomes less negative and at much higher frequencies it ultimately becomes positive (Fig.3(a)). An electron in an energy band may have positive or negative effective mass. At higher frequency where photo-thermal process is suppressed, is the state where the momentum transfer to the lattice from electron is smaller than the momentum transfer from the photon to the electron resulting positive (lighter) effective mass. At high chopping frequency the photo-thermal effects are suppressed and only II process will dominate the photconductivity. Therefore, at 3.9 kHz photo-current becomes positive which is due to the involvement of strongly correlated electrons in the VO₂. This process is summarized in Fig. 4. At 300 K, EQE is calculated for varying bias voltage and chopping frequency, Fig. 2(c). Interestingly, the band gap and used laser energy is optimum for MEG process at 300 K (room temperature). EQE as large as ~ 170% has been observed at room temperature. We would like to emphasize that EQE values may be further enhanced if one works with device fabrication styling where anti reflection coating is added and illuminated area is increased. In our experiment, illuminated area was only ~ 0.5 × 1 mm² and no anti-reflection coating was used.

In conclusion, photo-induced multiple exciton generation in insulating phase of VO₂ has been investigated by means of ac and dc photo-conductivity measurement methods. This is the first experimental assessment of the MEG driven EQE, IMT and sign of photo-generated carriers in VO₂. Our results show that the multiple carrier generation arising due to impact ionization in insulating state of the VO₂ depends upon the photon energy and relative strength of electron correlation. The electron correlation strength decreases with increasing temperature and provides a distinct advantage of choosing an appropriate laser energy or suitable temperature for working with low-MEG threshold. In VO₂, for 488 nm laser at room temperature the EQE is found to enhance up to as high as ~ 170%. At specific temperature (250 K) and beyond (< T_{IMT} ~ 340 K), photo-induced carrier multiplication is much higher and critical carrier density is achieved which resembles photo-induced IMT. The frequency dependent phase sensitive photo-current measurement has enabled the determination of sign of generated carriers. This study has presented underlying mechanisms of photo induced process in prototype strongly correlated material, VO₂, and paves a way for similar studies in other correlated electron systems. This
study may set off a new era of strongly correlated material based high-performance solar cell research.

Acknowledgements

DKS acknowledges support from SERB New Delhi, India in the form of early career research award (ECR/2017/000712).