The model of ultrafast light-induced insulator-metal phase transition in vanadium oxide

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Abstract. Ultrafast light-induced insulator-metal phase transitions (IM PT) in VO\textsubscript{2} thin films was studied with use of a pump-probe technique. These studies show that the IM PT could be realized via an intermediate state. The relaxation processes after optical pumping are dependent on pump energy. The excitonic controlled model for such type of IM PT is proposed on this basis. The main channel for the ultrafast light-induced IM PT is the resonant transition between excited states of correlated vibronic Wannier-Mott excitons (WME) in insulator phase and the unoccupied excited states in metallic phase. The experiment observation, such as pump power drastic dependences of relaxation could be interpreted in the framework of the model.

1. Introduction

Vanadium oxide (VO\textsubscript{2}) is well known model system for studies of IM PT. (see [1-6] and references therein). Special interest addressed here is the phenomenon of light induced ultrafast PT [7-10] which is in the order of $10^{-13}$ second time scale. Note that VO\textsubscript{2} is also an important material for optoelectronic applications.

In the present work we have performed a set of experiments for investigations of ultrafast light-induced insulator-metal (IM) phase transitions in different type of VO\textsubscript{2} thin films.

We manifest a new phenomenon in this context. It is the re-switching of the direction of relaxation process, which is dependent on optical pumping. In the low pump power case the relaxation process occurs only within the insulator phase while the higher power induces the relaxation from insulator to metallic phase. Based on these experimental data we suggest an intermediate state of the WMEs (hole containing V\textsuperscript{5+} cores with trapped electrons in large-radius state), which interacts with lattice becoming WME cluster under the cooperative “Negative-U” effect. This effect increases with pump energy (due to increased number of in–cluster WMEs). Along this line the main experimental results could be interpreted. It will be shown that the comparison of this theoretical approach with experimental data is favorable for exciton controlled model proposed.

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2. Relaxation in VO₂ thin films at different power pumping: experimental results

The optical pump-probe technique was applied to investigate the light-induced IM PT in the VO₂ thin films from femto- to nanosecond time scales. The wave lengths used for optical pumping and reflectivity measurements were 400 nm and 800 nm respectively. The measured time-resolved changes of the VO₂ reflectivity R were associated with light-induced IM PT in VO₂ in \(10^{-13}-10^{-9}\) sec time scale (figures 1a, 1b, see also ref. [10]).

\[\begin{array}{c}
\text{Figure 1. Measured transient reflectivity induced by different power laser pulses at room temperature for VO₂ thin film deposited on (a) MgO single crystal and (b) SiO₂ amorphous substrates, with the thickness ~ 200 nm and ~100 nm respectively.}
\end{array}\]

The laser pumping causes the transition into the equilibrium metallic phase. The excitation of the VO₂ film by sufficiently low laser power induces the reflectivity change with relatively fast back-relaxation to the values corresponded to the initial insulating phase. For instance, at pump power \(P\approx4\ mJ/cm^2\) for the VO₂ on MgO, and at \(\approx2\ mJ/cm^2\) for VO₂ on SiO₂ for room temperature case the back-relaxation process from excited to initial insulator state starts within monitored 3 ns time scale. Such a relatively fast back-relaxation was also confirmed in additional measurements of R, when the cw He-Ne laser radiation was applied as a probe. The relaxation time was estimated as <10 ns; however at the highest pump fluence the relaxation was about 500 ns. Lower energy laser pumping produces the relaxation of VO₂ system from an excited state back into insulator phase independently on the sample temperature, even if temperature corresponds to the middle of hysteresis loop. Very likely, such a behavior of VO₂ system is directly related to light-induced IM PT via some intermediate state. Such a conclusion is following from kinetic equations analysis. Moreover, we could expect some threshold behavior with respect to the transient occupation of the intermediate state. As it is seen from figures 1a, 1b the irreversible light-induced occupation of metallic phase states from initial insulating phase is clear appeared only in the case of pump power \(P\geq6\ mJ/cm^2\). The overcoming values correspond here to some definite change of the relaxation regime.

3. Light-induced ultrafast optical response in the framework of exciton controlled model: low pumping case

In accord with LDA (local density approximation) calculations made by R. Wentzcovitch et.al. [4], the ground state with monoclinic \(M_1\) structure in insulating VO₂-phase corresponds to an ordinary band Peierls insulator proposed by J.B. Goodenough [11]. This result was confirmed by recent important experiments of A. Cavalleri et. al. [8].
The most effective channel of ultrafast light-induced IM PT is related to three-stage process. This channel is based on the other active states involved in light-induced PT process, and becomes much more effective. In contrast to the first channel, after photogeneration of Frenkel exciton the following fast vibronic relaxation accompanied by phonon emission leads to the state filling of WME with large radius (significantly larger than the lattice constant). The electronic and vibrational states of the large-radius WME (V\(^{5+}\) hole center as a core + electron in the large-radius state) have rather similar parameter values with respect to the final, metallic phase state of VO\(_2\). Indeed, the large-radius electronic states of WMEs are similar to the intermediate states for the formation of “V\(^{5+}\) + extended radius electron” state in metallic phase, which finally form corresponding metallic state due to their good overlapping. Moreover, these two states corresponding to the IM transition have the vibration wave functions which are mainly formed both by approximately the same pronounce suppression of the distorted oxygen ion hexahedron in the surrounding of each V\(^{5+}\) ion. The latter is due to Coulomb extra-attraction induced by charge separation under the conditions of large radius electronic state appearance. That is, the equilibrium local lattice distortions in these two states are also similar. Last not least, owing to relatively long life time of vibronic WME the photoinduced population of WME states could be sufficiently high in order to produce the transition into metallic phase. As a result, the third final stage in this process is the high flow of probability resonance transition from WME ground state in the insulating phase into unoccupied excited metallic phase state. This process has \(\sim 10^{-13}\) sec characteristic time scale. In contrast to the first channel case discussed above, the matrix element for such a resonance transition has small enough vibronic reduction. In addition, sufficiently high concentration of initial vibronic WMEs is realized. These circumstances allow us to consider such a channel as the main candidate for the light-induced ultrafast IM PT in VO\(_2\). Let us discuss the experiment explanation in such a case.

First note that, in the case of low optical pumping, some excited intermediate state is occupied by light. It could be vibronic WME state. Nevertheless, after its occupation the strong back-relaxation into insulating ground state dominates and does not allow to realize the IM PT by sufficiently low pumping (P < 6 \(\mu\)J/cm\(^2\), see figures 1a, 1b), as mentioned above. That is, here we only detect the transient reflectivity related to ultrafast occupation of intermediate excited states which could be active in light-induced IM PT but for the pumping case with more high power magnitude.

Second, the radiative recombination relaxation could appear after optical pumping. Such a process corresponds to vibronic WMEs recombination. This radiative relaxation is directed back to the initial insulating phase. It could be the main relaxation channel in the case of low optical pumping (P < 6 \(\mu\)J/cm\(^2\)) in accordance with the experiment (see figure 1b for the case of VO\(_2\) film on the amorphous SiO\(_2\) substrate).

4. Light-induced phase transition mechanism in the framework of exciton controlled model: high optical pumping

The observed phenomenon of light-induced IM PT in VO\(_2\) thin films realizing for the case of sufficiently high pump power (as > 6 \(\mu\)J/cm\(^2\) for VO\(_2\) thin films under discussion) could be explained in terms of the exciton controlled model. As before we will use the band-like description of insulator and metal phases taking into account related results of Goodenough [11], Wentzcovitch et al [4], and Cavalleri et al [7,8]. In addition to the previous paragraph approach we take into account some cooperative effect for the case of pump power increase. Such an effect is related to indirect WME-WME interaction within WME-cluster, and results in formation of the in-cluster WME states. The increase of WME in-cluster number causes the lowering of WME cluster state energy due to vibronic interaction in the framework of co-operative “Negative-U” effect. In this case the WME number will have a profound influence on evolution of the WME-cluster considered as intermediate state for ultrafast light-induced phase transition.

The scheme for light-induced processes leading to the IM PT are presented in Figure 2 for the case of high enough pump power respectively. The latter scheme assumes realization of the WME clustering after optical pumping. The electron-lattice states including the vibronic WME (figure 2) are key point. Different adiabatic potential branches related to different vibronic states (as \(d_{||}\) - valence
band and WME states, figure 2) are presented in harmonic approximation. But they could be under the conditions of resulting anti-crossing behavior when the potential curves of the different vibronic states initially tend to crossing (it is the case of the vibronic WME cluster state and $d_{||}$ - valence band state depicted in figure 2).

![Diagram of light-induced insulator-metal phase transition and related processes](image)

**Figure 2.** The scheme of light-induced insulator-metal phase transition and related processes (the main one is via vibronic Wannier-Mott Exciton clusters, channel 7 in VO$_2$: the case of high optical pumping. Optically excited Charge Transfer Vibronic Exciton phase (channels 1*,2*) becomes in resonance with metallic phase.

The first stage of PT is optical pumping of Frenkel exciton and of excited WME states (figure 2, transitions “1”, “4” respectively). Subsequently, the relaxation from Frenkel exciton and from excited WME states into the ground WME state (transitions “2”, “3”, “6”) occurs along with weak direct tunnel transitions into metallic phase (transition “5”). Nevertheless the main channel of light-induced PT is caused by resonance tunneling from intermediate photoexcited WME cluster state in insulator phase into excited state (unfilled) in metallic phase (transition “7”). Namely this process is considered here as a light-induced mechanism of the IM PT in pure VO$_2$.

Note that above-mentioned intermediate WME-cluster state depends on the pump power and on the proximity to critical temperature. Such a dependence occurs because WME state energy within the cluster depends on number of WMEs. As a result, the WME-cluster energy level could be controlled by optical pumping due to sufficiently strong interaction between vibronic WMEs on the one hand, and breathing mode and IM PT order parameters on the other.
Indeed, the indirect interactions between different vibronic WMEs via soft mode provide the correlations defined as cooperative “Negative-U” effect. In this conception, an increase of the number of photoexcited vibronic WMEs with pump power will lead to formation of cooperative excitonic potential well. Its depth has pronounced, super-linear increasing per single vibronic WME with number \( N \) of in-cluster photoexcited vibronic WMEs. So, we could obtain \( E_{\text{WME}} \approx -A^* - NB^*(N,T) \) in the framework of a scenario proposed. Here the \( A^* \) parameter corresponds to single vibronic WME energy, while parameter \( B^*(N,T) \) is related to the cooperative in–cluster vibronic contribution of all WMEs to the energy of single WME in the cluster.

Along this way the value of threshold pump power corresponded to the change of the relaxation direction optical pumping (from back-relaxation into the initial insulating phase to relaxation into new metallic one) is appeared in accord with the experiment.

Namely, the depth of co-operative potential well of vibronic WME cluster significantly increases with pump power as well as with tending of the temperature to critical temperature (renormalized by pumping). Such a deepening of the potential well is responsible here for the change of the relaxation direction with pump power increase or with temperature tending to the critical temperature in the PT region. As a result, the back-relaxation into insulator phase is switched to the relaxation towards metallic phase. This switching occurs due to suppressing of the back-relaxation from excited intermediate state to initial insulator state due to forbidden Frank-Condon type radiative recombination. Here the light-induced PT from insulating to metallic phase could be realized only for the pump power which is higher than a threshold value (for \( P \geq 6 \text{ mJ/cm}^2 \) for thin film thickness ~ 100 nm, and with amorphous SiO\(_2\) substrate).

Note that well known effect of insulator-metal transition inducing by carriers (due to additional electrons or holes liberation from defects including their thermo-inducing, or due to carrier injection) could be explained as a result of a decrease (up to sign change to its negative value) of the free energy expansion coefficient for charge transfer harmonic fluctuations. Such a behavior \[12\] is related with increase of carrier induced screening of the charge separation accompanied by pronounce softening of the charge transfer conditions. The latter circumstance could switch on the charge transfer mechanism of insulator-metal phase transition inducing.

5. Conclusions

The proposed exciton controlled model of light-induced IM PT allows explaining the main features of the light-induced ultrafast (in femtosecond time scale) IM PT and its relaxation kinetics in VO\(_2\) thin films. For instance, it explains the nature and key role of PT phenomenon via specific intermediate states related to vibronic Wannier-Mott excitons cooperated in clusters. Such excitons are essentially interacting with lattice leading to in-cluster cooperative “Negative-U” effect. This effect is responsible for uncommon dependences of the relaxation kinetics in VO\(_2\) at different optical pumping.

6. Acknowledgements

This work was supported by US-DOD-W911NF-04-1-0019, by NASA-NCC5-518, and by ARO-DAAD19-02-1-0298.

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