Selectivity of the photoexcited metal-semiconductor phase transition in vanadium dioxide initiated by picosecond pulses

A. A. Bugaev, V. V. Gudyalis, B. P. Zakharchenya, and F. A. Chudnovskiĭ
A. F. Ioffe Physicotechnical Institute, Academy of Sciences of the USSR

(Submitted 20 August 1981)

Pis'ma Zh. Eksp. Teor. Fiz. **34**, No. 8, 452–455 (20 October 1981)

The results of a study of the kinetics of a metal-semiconductor phase transition (MSPT) in vanadium dioxide, which is excited by picosecond laser pulses with a quantum energy of 1.17 and 2.34 eV, are presented.

PACS numbers: 72.60. + g

The results of mode self-locking, which was obtained by using a nonlinear element consisting of a vanadium dioxide film, were published in Ref. 1. They showed that the kinetics of the MSPT produced as a result of excitation by short ($\leqslant 10^{-9}$ sec) laser pulses are not related to the kinetics of the temperature increase of the film. For this reason, we have investigated the development of MSPT in the picosecond time interval with a time resolution of 6×10^{-12} sec. The studies were carried out with the aid of a generator of 6×10^{-12}-sec, single picosecond pulses, using the method of time probing with preliminary excitation.[2] The ratio of the intensities of the probing and excitation beams is $1{:}10^3$. The controlled parameter is the variation of the reflection coefficient of the investigated film. We performed two different experiments. In one of the experiments the MSPT in the vanadium-dioxide film was excited by a wavelength $\lambda = 1.06$ μm ($\hbar\omega = 1.17$ eV), and in the other experiment by a wavelength $\lambda = 0.53$ μm ($\hbar\omega = 2.34$ eV). In these experiments the excited MSPT was probed only at the wavelength $\lambda = 1.06$ μm. In both cases the excitation-energy density was the same and equal to 3–5 mJ/cm^2.

The object of our study was an oxidized vanadium film,[3,4] which was prepared in the following manner. Layers of aluminum (~1000 Å thick) and vanadium (300–400 Å) were deposited successively by thermal evaporation in a vacuum onto a devitrified-glass substrate. The resulting structure was then annealed in air at a temperature of 450–500 °C, so that an oxidized vanadium film was formed on the surface that contained VO_2 in addition to other vanadium oxides. The oxide film for the investigation was not chosen randomly. A stoichiometric VO_2 film that is placed on a transparent substrate reveals a small change in the optical properties (transmission or reflection) during the MSPT. This seriously restricts the accuracy of the measurements. On the other hand, an oxidized vanadium film that is placed on a reflecting layer of aluminum provides, for example, at $\lambda = 1.06$ μm a change in the reflection coefficient from 3 to 53% during the MSPT, because of the interference nature of the reflection. To describe the investigated oxide film more completely, Fig. 1 shows the spectral variation of the reflection coefficient in the metallic and semiconductor states, as well as the temperature hysteresis loop. Although the properties of the

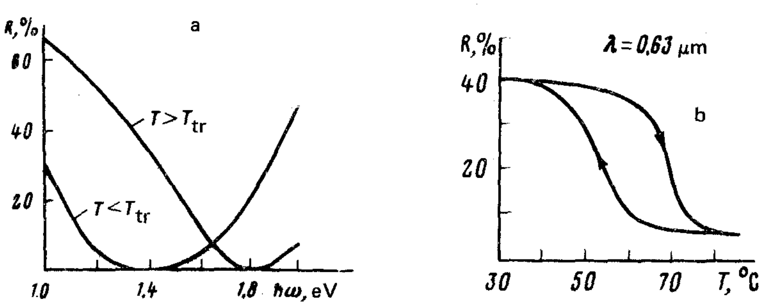

FIG. 1. Spectral dependence of the reflection coefficient of an oxidized vanadium film (a) and the temperature hysteresis loop (b). The incidence angle is ~10°.

oxidized vanadium film[3,4] are identical to those of a stoichiometric VO_2 film, we nevertheless performed identical experiments with both the former and the latter. The time-dependent behavior of the MSPT in a vanadium oxide film obtained in the experiments is shown in Fig. 2. The main results are as follows: 1) for excitation by picosecond laser pulses with a quantum energy of 1.17 eV, the MSPT is initiated in a time $\leqslant 10^{-12}$ sec; 2) for excitation by a pulse with a quantum energy of 2.34 eV the MSPT occurs with a delay of $\sim 10^{-9}$ sec; 3) the reflection coefficient for excitation with $\hbar\omega = 1.17$ eV at $\tau \leqslant (5\text{–}7) \times 10^{-10}$ sec for the various samples can be less than or equal to the reflection coefficient for the metallic state, but never larger; 4) analogous results were also obtained for a stoichiometric VO_2 film, which was placed on a quartz substrate.

Below, we present arguments, which, in our opinion, can explain the obtained results. According to Refs. 5–7, the energy spectrum of VO_2 can be represented qualitatively in the following manner (see Fig. 3). In the metallic state ($T > T_{tr}$ is the phase-transition temperature) the Fermi level lies in the double degenerate, narrow $d_{||}$ band, which originates from d orbitals that overlap each other along the "C" axis of the crystal. This band is overlapped by a wider π^* band, which is formed by d orbitals directed toward the oxygen atoms and hybridized with the $p\pi$ orbitals of oxygen. In the semiconductor phase ($T < T_{tr}$) the π^* band rises above the Fermi level, and the degenerate $d_{||}$ band drops. Destabilization of the π^* band is usually

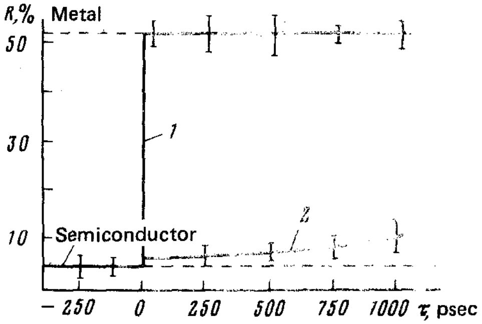

FIG. 2. Kinetics of phase-transition in oxidized vanadium film. 1–Excitation with $\hbar\omega = 1.17$ eV, 2–excitation with $\hbar\omega = 2.34$ eV. The reflection coefficient values in the metallic and semiconductor states are denoted by dashed lines.

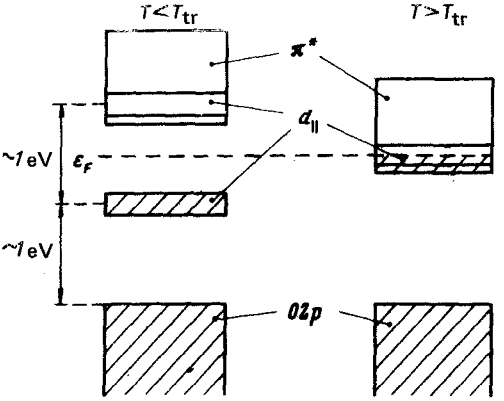

FIG. 3. Qualitative band structure of VO_2. ϵ_F is the Fermi level.

attributed to a displacement of the vanadium atoms from the center of the oxygen octahedron (the antiferroelectric component of the distortion or "twisting"). The splitting of the $d_{||}$ band is attributed to two factors: pairing of V^{4+} - V^{4+} atoms along the "*C*" axis (Peierls effect) and the appearance of a correlation gap (Mott-Hubbard effect).

There are serious reasons for assuming that the correlation interaction accounts for the major contribution to the splitting energy of the *d* band. According to various estimates, the Mott-Hubbard gap in VO_2 lies within the limits of 1.0 to 1.5 eV.[8–10] According to the data of Ref. 11, it has a value of ~1.22 eV.

Thus, excitation with a 1.17-eV quantum energy leads to the formation of a *d-d* electron-hole plasma, which initiates the MSPT by changing the correlation gap as well as that part of the gap (apparently a small part) which is attributable to the V^{4+} - V^{4+} pairing. The MSPT initiation time of $\leqslant 10^{-12}$ sec obtained in our experiments makes it possible to state that for photoexcitation of the *d-d* electron-hole plasma the MSPT does not occur in accordance with the "normal" thermal mechanism, when the photoexcited electrons heat the lattice to the phase-transition temperature T_{tr} by energy relaxation and nonradiative recombination. In fact, the phonon-diffusion times are always less than the propagation velocity of sound v_s, and for a film of thickness *d* they cannot be less than $d/v_s \sim 10^{-5}$ (cm)/10^5 (cm/sec) = 10^{-10} sec.

A different situation exists for photoexcitation of the MSPT by a quantum with an energy of 2.34 eV. Here the electron production occurs in the $d_{||}$ band and the hole production occurs in the lower-lying O2*p* band. The appearance of an electron-hole plasma consisting of *d* electrons and *p* holes, unlike the *d-d* electron-hole plasma, does not lead to a change of the correlation gap until the *p* holes undergo energy relaxation and are transformed into *d* holes. This relaxation time may be the cause of the observed delay time, which is less than or of the order of 10^{-9} sec. On the other hand, relaxation of the hot holes leads to the production of phonons and film heating. Therefore, the "normal" thermal mechanism must be included under these conditions. A slight increase of the reflection coefficient for times

$\tau < 5 \times 10^{-10}$ sec ($\hbar\omega = 2.34$ eV) is attributable to a change of the dielectric constant due to an increase of the free-carrier density in the conduction band of the VO_2 film in the semiconductor state.

At present, we cannot explain the fact that at a quantum energy of 1.17 eV a change of the reflection coefficient corresponding to a complete MSPT is not realized in all samples. This may be due to the fact that all of the illuminated region is not immediately transformed into the metallic state, either because a trivial nonuniformity of the film that occurs during the preparation or because of the formation of electron-hole drops. We note that the uniform film illumination was monitored individually. This question requires further investigation.

Thus, the MSPT in VO_2 can be initiated in a time less than 10^{-12} sec and it can be accomplished without heating the lattice to the MSPT temperature. This fact, as well as the selective nature of the observed effect, indicate that the electron-hole plasma plays a large role in the *d-d* bands in the VO_2 phase-transition mechanism.

The authors are deeply grateful to A. G. Aronov for enlightening discussions of the results of this work.

1. A. A. Bugaev, B. P. Zakharchenya, and F. A. Chudnovskiĭ, Pis'ma Zh. Eksp. Teor. Fiz. **33**, 643 (1981) [JETP Lett. **33**, 629 (1981)].
2. E. Ippen and Ch. Shenk, Measurement methods, In: Sverkhkorotkie svetovye impul'sy (Ultrashort Light Pulses), Ed. S. Shapiro, Mir, Moscow, 1981.
3. A. A. Bugaev, B. P. Zakharchenya, and F. A. Chudnovskiĭ, Kvantovaya Elektron. **6**, 1459 (1979) [Sov. J. Quantum Electron. 9, 855 (1979)].
4. A. A. Bugaev, B. P. Zakharchenya, and F. A. Chudnovskiĭ, Fazovyĭ perekhod metallapoluprovodnik i ego primenenie (Metal-Semiconductor Phase Transition and its Application), Nauka, Leningrad, 1979.
5. J. B. Goodenogh, Proc. Tenth Conf. on Phys. of Semicond. Ed. S. P. Keller, J. C. Hensel, and F. Stern, Boston, 1970, p. 304.
6. E. Caruthers, L. Kleinman, and H. J. Zhang, Phys. Rev. **137**, 3753 (1973).
7. N. Sommers, R. De Groot, D. Kaplan, and A. Zylberstein, J. Phys. Lett. **36**, 157 (1975).
8. T. M. Rice, D. B. McWhan, and W. F. Brinkman, Proc. Tenth Conf. on Phys. of Semicond., Ed. S. P. Keller, J. C. Hensel, and F. Stern, Boston, 1970, p. 293.
9. A. Zylberstein and N. F. Mott, Phys. Rev. **B 11**, 4383 (1975).
10. D. Paquet and P. Leroux-Hugon, Phys. Rev. **B 22**, 1284 (1980).
11. C. Sommers and S. Doniach, Solid State Commun. 28, 133 (1978).

Translated by Eugene R. Heath
Edited by S. J. Amoretty