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G Stefanovich, A Pergament and D Stefanovich

Petrozavodsk State University, Petrozavodsk, 185640, Russian Federation

Abstract.   In this paper the problem of the Mott metal–insulator transition in vanadium dioxide driven by an external electric field is considered. Delay time (t_d) measurements have shown that the experimental value of t_d is almost three orders of magnitude lower than the theoretical value, calculated in a simple electrothermal model. This suggests that under non-equilibrium conditions (in high electric fields) electron correlation effects contribute to the development of the insulator to metal transition. The extra-carrier injection from Si into VO$_2$ was carried out in the structures Si–SiO$_2$–VO$_2$ on p-type silicon with $\rho = 0.1$ Ω cm and a SiO$_2$ thickness 70 nm. It has been shown that the metal–insulator transition in VO$_2$ can be initiated by injection, i.e. by the increase of the electron density. The value of the critical density was found to be of the order of the electron density in VO$_2$ in the semiconducting phase, approximately 10^{18}–10^{19} cm^{-3}. This confirms that the metal–insulator transition in VO$_2$ is the purely electronic Mott–Hubbard transition.

1. Introduction

In the field of the physics of phase transitions, metal–insulator transitions (MITs) play a special role. First, the MIT is a problem of considerable interest, because it is concerned with a wide range of issues from the metallization of stars to the size-induced transition in small clusters of metals [1]. The MIT can arise from one of many causes; for example, the transitions found in condensed matter systems are the following: compositionally induced, temperature or pressure induced and some other (e.g. those induced by magnetic or electric fields). Well known examples of such systems are doped semiconductors, some transition metal compounds (for instance, several vanadium oxides [2, 3]), high-T_c superconductors, etc.

Generally, MITs are divided into two groups according to the mechanism assumed: either structural or electronic. In the first category, some change in the crystal lattice (structural phase transition) leads to a splitting of the electronic conduction band and hence to a MIT. In the second category, the transition is purely electronic in origin and can be described by the models in which the lattice is fixed or even altogether absent, as in the 'jellium' model. Mott's original idea [2] of the transition triggered by electronic correlations was based on the model of an array of atomic potentials with one electron per atom and a Coulomb interaction between the electrons. For a sufficiently small lattice spacing (or high electron density) the ion cores will be screened and the system will be metallic. For a lattice spacing larger than a critical value, the screening will break down and the system will undergo a first-order phase transition to an insulator. The Mott criterion for the electronic transition is given by [1, 2]:

$$(n_c)^{1/3}\alpha_H \approx 0.25 \tag{1}$$

where n_c is the critical density and α_H is the Bohr radius.

Vanadium dioxide undergoes a metal–insulator phase transition at $T_t = 340$ K (the transition temperature) and there is still no consensus of the description of the driving

mechanism of this transition—either electron correlation effects or structural instabilities [4, 5]. Also, electrical switching due to MITs has been reported for planar thin-film and single-crystal VO$_2$-based structures [3, 6, 7]. The S-shaped voltage–current characteristic is conditioned by the development of an electrothermal instability in the switching channel. When a voltage is applied, the channel is heated up to $T = T_t$ (at $V = V_{th}$, where V_{th} is the threshold voltage) by the current and the structure undergoes a transition from a high-resistance (OFF) insulating state to a low-resistance (ON) metallic state.

Electrical switching of a kind can be observed in a great variety of materials in many different forms and structures [7]. The voltage–current characteristics of such systems are usually classified into two categories: those with S-type and with N-type negative differential resistance (NDR). The shape of these current–voltage curves (S or N type) depends on many factors [7–9]. Moreover, the form of the voltage–current characteristic can be essentially unusual, as has been observed for the V$_2$O$_3$:Cr system exhibited the combined 'S to N' switching [9].

In [10], we report on the switching in sandwich, metal/oxide/metal (MOM), structures based on vanadium dioxide thin films obtained by anodic oxidation. In this case (i.e. in high electric fields, 10^5–10^6 V cm^{-1}), the possible influence of electronic effects on the MIT should be taken into consideration. Electronic effect on the MIT consist of a field-induced increase in the charge carrier density, which should screen Coulomb interactions [11], leading to the elimination of the Mott–Hubbard energy gap at $T < T_t$. This type of switching mechanism, involving the 'field-induced' Mott transition, has been also proposed for other transition metal oxides [11–13].

In the present paper we report on delay time measurements carried out on VO$_2$-based MOM structures. Also, the influence of the carrier injection on switching and MIT in vanadium dioxide has been studied using planar switching devices. The objective of this work was to clarify the physical mechanism of the MIT in VO$_2$.

2. Experimental details

The sandwich devices under study were fabricated by the anodic oxidation [13, 14] of the vanadium metal substrates–vacuum-deposited vanadium layers. Metal (gold) electrodes were evaporated onto the surfaces of the oxide films to complete the MOM structure (figure 1(a)). Spring-loaded point contacts (gilded wire 0.5 mm in diameter) were also used. Channels consisting of the vanadium dioxide phase were formed in the initial anodic films during the process of electroforming [13].

The oxidation was carried out electrochemically, under anodic polarization in an electrolyte. The thickness of the oxide films, d, was about 200 nm. Details of the preparation technique, as well as some experimental procedures, concerning the switching measurements, have been described previously [10, 13].

The injection of electrons from Si into the VO$_2$ we carried out in the structures Si–SiO$_2$–VO$_2$ (figure 2) on p-type silicon with $\rho = 0.1$ Ω cm and a silicon dioxide layer thickness $d_I = 70$ nm. The planar switching devices were fabricated using a sol–gel technique, which was similar to that proposed in [15]. In this method, V$_2$O$_5$ was placed in a ceramic boat and heated in air at 900 °C (above the melting point, 690 °C) for 1 h and then quenched by pouring the molten oxide into room-temperature distilled water. After cooling down, a few millimetres of this gel solution were placed onto a Si–SiO$_2$ substrate and the excess solvent was allowed to evaporate at $T = 100$–120 °C. As a result, yellowish-brown films were prepared with thicknesses of the order of 0.1–1 μm. Aluminium electrical contacts were obtained by thermal vacuum evaporation. The structures had approximately a 0.2 mm gap between the Al contacts.
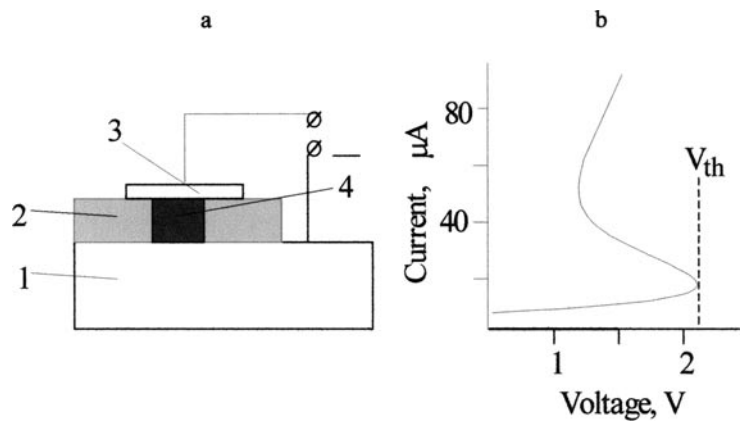
Figure 1. (a) Schematic diagram of the sandwich structure: 1, vanadium; 2, vanadium oxide film; 3, gold electrical contact; and 4, VO$_2$ channel. (b) The voltage-current characteristic.
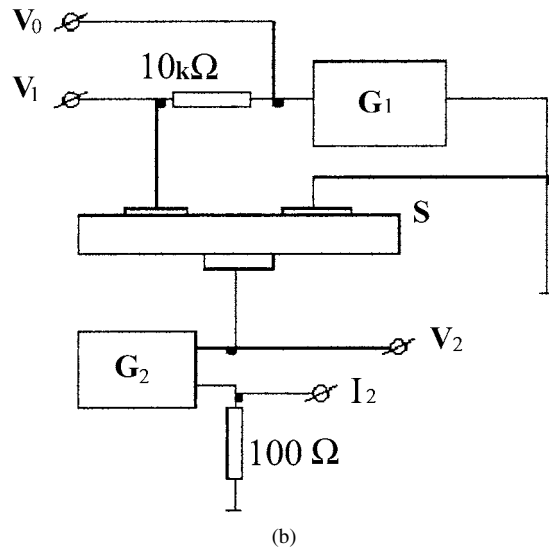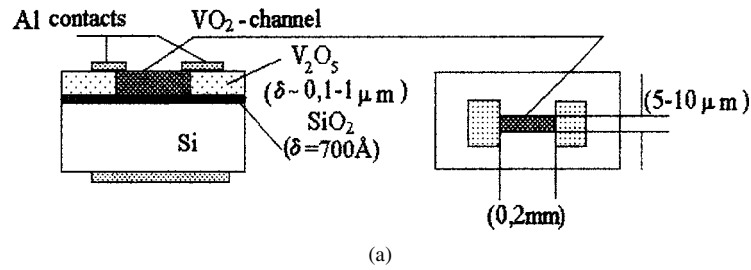
Figure 2. (a) Schematic diagram of the planar structure on Si and (b) the injection experiment scheme: G$_1$, square pulse generator; G$_2$, ramp generator of a linearly changed voltage (maximum amplitude $V_0 \sim 100$ V); S, Si–SiO$_2$–VO$_2$ sample (see (a)). The voltages V_0, V_1 and V_2 and the current I_2 were measured by a two-beam four-input oscilloscope.

After the process of electroforming [10, 13, 15], the voltage–current characteristics of the devices become S shaped. As the temperature increased, the switching threshold voltage V_{th}
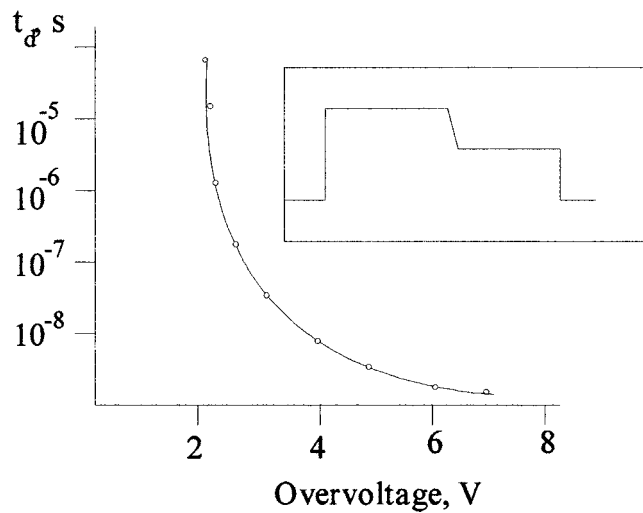
Figure 3. Delay time as a function of applied voltage and (inset) $V(t)$ oscillogram.

decreased to zero at a certain critical temperature. This temperature was found to be practically equal to the transition temperature for vanadium dioxide $T_t = 340$ K. At $T > T_t$ the switching effect no longer occurred. This indicated that in both cases (sandwich and co-planar devices) the channels, consisting of pure and stoichiometric VO_2, were formed during electroforming. No special characterization of the initial films had been conducted. Some details, as well as the corresponding references, concerning the quality, structure and composition of the films, can be found in [15] (sol–gel) and [10, 13, 14] (anodic films).

## 3. Results and discussion

3.1. Delay time measurements

The voltage–current characteristic of the MOM structure is shown in figure 1(b). These characteristics are S shaped and the threshold parameters (V_{th} and I_{th}) vary slightly from sample to sample. Normally, the threshold voltage is of the order of 1–10 V and the threshold current is 10–100 μA.

When the structures are switched with rectangular voltage pulses, they are characterized by a certain delay time t_d. The value of t_d strongly depends on the applied voltage; $t_d \to \infty$ as V approaches the dc V_{th} value and it sharply decreases as the pulse amplitude rises (figure 3).

We then investigated the utility of a simple thermal model in estimating the switching time. The minimum delay time (i.e. the time required for the switching channel temperature to rise from the ambient, T_o, to the equilibrium transition temperature $T_t = 340$ K, without taking into account any heat dissipation) may be found from the heat balance equation:

$$t_{d,min} = c\rho\Omega_s(T_t - T_o)/VI \tag{2}$$

where $\Omega_s = \pi r^2 d$ is the channel volume of the sandwich structure (the channel radius, r, is equal to about 1 μm [10]), $c = 690$ J kg^{-1} K^{-1} and $\rho = 4340$ kg m^{-3} [16] are, respectively, the heat capacity and the density of vanadium dioxide. For $V = 6.8$ V and a current which was measured to be $I = 57$ μA (see figures 3 and 1(b)), equation (2) yielded $t_{d,min} = 0.9$ μs $= 900$ ns, while the experimental value of t_d at this voltage was
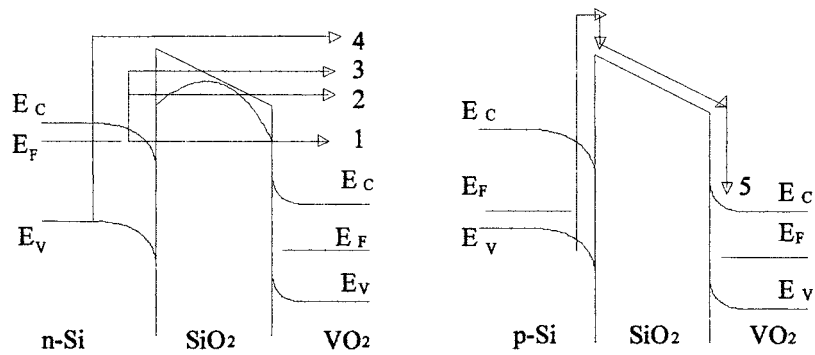
Figure 4. Different kinds of injection in the MIS structure: 1, tunnel injection; 2, field-assisted (thermal-auto-electron) injection; 3, thermal-electron injection; 4, photo-injection; and 5, avalanche injection.

only 1.5 ns (figure 3). For more precise calculations, it is necessary to take into consideration the current filament and domain formation effects [6]. This might change the above estimates, but only slightly: the difference between the theoretical and experimental values of t_d are too high, almost three orders of magnitude.

Thus, under non-equilibrium conditions (in high fields), the switching effect is not described in terms of the simple electrothermal model. Such a conclusion has also been made in some previous investigations of switching in vanadium dioxide [6, 10, 13]. For a more detailed understanding it is important to take the electron correlation effects into account, which may contribute to the development of the insulator to metal transition in high electric fields.

3.2. Influence of carrier injection on the MIT in VO$_2$

The extra-carrier injection into a semiconductor of a metal–insulator–semiconductor (MIS) structure may be brought about in several ways. As depicted in figure 4, is may be by tunnelling, thermal-electron (or auto-thermal-electron, i.e. field-assisted) injection, avalanche injection and photo-injection. The avalanche injection seems to be the most effective, because in this case one can reach the maximum magnitude of the injection current in comparatively low electric fields. For example, for p-Si with $\rho = 0.1 \, \Omega$ cm and SiO$_2$ thickness $d_I = 100$ nm, avalanche breakdown of the space charge region (SCR) begins at $\psi_s = 6.1$ V and $V_G = 20$ V, where ψ_s and V_G are the surface potential and the gate voltage, respectively. In addition, as the result of the SCR avalanche breakdown, in very high electric fields, electrons become hot; a region with quasi-Maxwellian distribution of hot electrons occurs near the semiconductor–insulator junction [7]. This distribution corresponds to an electron temperature of about 2000 K; therefore, almost all injected electrons reach the VO$_2$, passing through the silicon dioxide layer.

For the injection experiments, rectangular voltage pulses (with amplitude V_0 and duration τ_0) from the generator G1 (figure 2(b)) were used to switch the structure. When $V_1 > V_{th}$, the delay time depends on V, as in the case of sandwich structures. The avalanche injection of electrons was carried out by means of the negative V_2 voltage from the ramp generator G2. The current through the structure, I_2, was determined by measuring the voltage across the resistor $R_2 = 100 \, \Omega$. When the value of V_2 achieved the voltage of the avalanche injection (at $t = t_2$), a narrow current peak on the oscillogram $I(t)$ appeared. Its magnitude was $I_2 \sim 0.3$–3 mA and its 'width' was $\tau_2 \sim 100$ ns $\ll \tau_0$ (figure 5(b)).
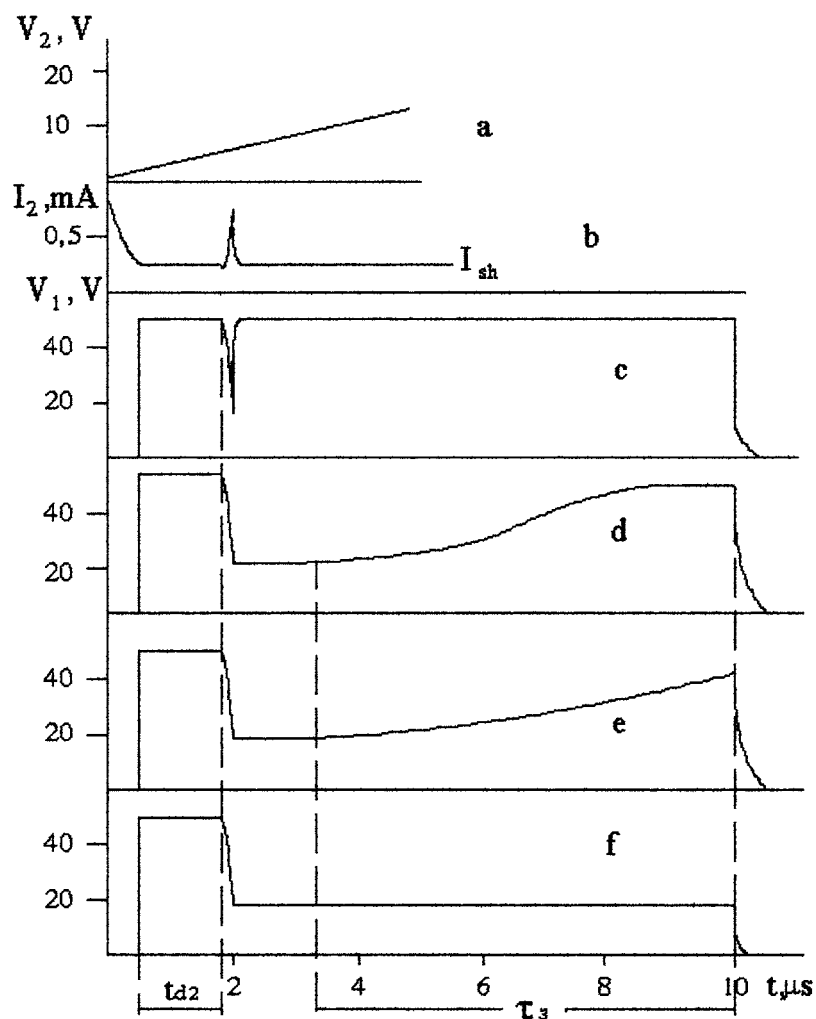
Figure 5. Injection oscillograms: (a) the substrate voltage (V_2); (b) the current in the substrate circuit, I_{sh} is the shift current due to the capacity charging by V_2; and (c)–(f) voltage pulses across the VO$_2$ channel at different values of V_0 ($V_{0c} < V_{0d} < V_{0e} < V_{0f}$).

When applying the switching and injection pulses simultaneously, it was found that even if either $V_1 < V_{th}$ or $\tau_0 < t_d$ (i.e. in the OFF state), the structure could be switched into the ON state by the I_2 pulse, i.e. by injection of electrons into the vanadium dioxide. In this case, the delay time (t_{d2}) did not depend on V_1 and it was determined only by the shift of the I_2 pulse with regard to the front edge of the V_0 pulse, i.e. by the value of t_2—see figure 5.

We next investigate the effect of the V_0 amplitude upon the behaviour of the structure. If the value of V_0 is sufficiently low, the structure switches on for the time τ_{ON}, which is not longer than the injection current pulse duration, $\tau_{ON} < \tau_2$ (figure 5(c)). An increase of V_0 leads to τ_{ON} to become independent of τ_2 and it is determined only by the value of V_1, $\tau_{ON} \gg \tau_2$ (figures 5(d)–5(f)). Also, in the ON to OFF transition, a slow component appears with a characteristic time $\tau_3 \sim 10$–20 μs. This recovery time is of the order of the recovery time measured in standard switching experiments, without injection (at $V_1 > V_{th}$,

using the double-pulse technique [11]). Note that the transition from the first behaviour (fast recovery, figure 5(c)) to the second behaviour (slow recovery, figure 5(d)) is rather sharp, not monotonous.

It is to be emphasized that the ON-state resistance does not change in this case (i.e. during the transition from the 'fast' to 'slow' recovery time behaviour). The increase of V_1 is completely determined only by the change of the output voltage V_0.

When the voltage pulse V_2 was positive, no switching was observed at any values of $V_1 < V_{th}$. If, however, V_1 was greater than V_{th}, it was possible to switch off the structure by applying a certain voltage V_2. The characteristic time of this process was much shorter than τ_3, the characteristic time of the slow component of the recovery time.

The described effect cannot be explained by the conventional current-induced Joule heating, because all the structures had negligible leakage currents ($I < 10^{-12}$ A at $V = 60$ V). Moreover, in the electrothermal model, it would be difficult to understand why the effect strongly depends on the polarity of the V_2 pulse. Heating by the current of the injected carriers is also impossible because $\tau_2 < t_d$. In addition, the fact that the switching (and, hence, MIT) mechanism is electronic rather than thermal is suggested by the short component in the recovery time (figure 5(c)).

3.3. Mechanism of metal-insulator transition in VO$_2$

It has been shown [10] that under non-equilibrium conditions the switching is not described in terms of the simple electrothermal model and electron correlation effects do play an important role in the development of the insulator to metal transition in VO$_2$ in high electric fields. This conclusion is also supported by the results presented in section 3.1. Finally, injection experiments, described in section 3.2, directly show that the non-equilibrium electrons injected from outside (Si substrate, for example) can initiate switching—and, consequently, the MIT— in VO$_2$ at a certain critical electron density n_c. (This effect may also be treated as a lowering of T_t due to an excess negative charge. A similar situation takes place at the metal–semiconductor interface Schottky barrier [6]. In such a case a positive space charge enhances the stability of the VO$_2$ semiconducting phase, thus increasing its transition temperature.)

For the Mott transition, the values of n_c one can find from equation (1):

$$n_c = (0.25/\alpha_H)^3 \approx 3 \times 10^{18} \text{ cm}^{-3} \tag{3}$$

where $\alpha_H = \hbar^2 \varepsilon / m^* e^2$, ε is the dielectric constant ($\sim$100 for VO$_2$ [17]), $\hbar$ is the Planck constant and m^* and e are, respectively, the effective mass and charge of an electron. For vanadium dioxide $m^* \approx 3m$ [2].

We also estimated the value of n_c from our injection experiments. The total charge passing through the structure is approximately equal to $I_2\tau_2$. The channel volume Ω_p (see figure 2(a)) for one of the samples was measured to be $\Omega_p = 1.3 \times 10^{-10}$ cm^3, and the current was $I_2 = 0.9$ mA. Thus, the charge density injected from Si into VO$_2$ is

$$n_{inj} = I_2\tau_2/e\Omega_p = 4.3 \times 10^{18} \text{ cm}^{-3}. \tag{4}$$

This value is in excellent agreement with the above-obtained theoretical estimate (3×10^{18} cm^{-3}). Furthermore, both these numbers practically coincide with the carrier density in the semiconducting phase of VO$_2$ at $T \rightarrow T_t : n_s \sim 10^{18}$–$10^{19}$ cm^{-3} [2].

It is important to note that the value of n_c is much less than the electron density in the metallic phase of VO$_2$ ($n_m = 10^{22}$–10^{23} cm^{-3} [2]). Therefore, the obtained results may not be accounted for merely by a sharp increase in the switching channel conductivity due to the pumping up of a sufficiently high carrier density to the conduction band of the material.

Thus, there is no doubt, from these experiments, that the insulator to metal transition in vanadium dioxide can be initiated by an increase of charge carrier (electron) density without heating the lattice up to $T = T_t$. The value of the critical density n_c was found to be of the order of electron density in VO$_2$ just below the transition point, i.e. $n_c \sim n_s \sim 10^{18}$–$10^{19}$ cm^{-3}. This confirms that the MIT in VO$_2$ is rather of the Mott–Hubbard type.

4. Conclusion

To summarize, the results obtained in the present work show that the experimental value of t_d was measured to be 1.5 ns$\times 10^{-9}$ s. On the other hand, within the model of 'critical temperature', the minimum delay time under the same conditions should be approximately 10^{-6} s. Thus, under non-equilibrium conditions, the switching effect does not seem to be described in terms of the simple thermal model and electron correlation effects contribute to the development of the MIT under high electric fields in vanadium dioxide. In order to verify this hypothesis, we have carried out some additional experiments.

It has been shown that the MIT in VO$_2$ can be initiated by injection, i.e. by an increase of the electron density without heating the lattice to $T = T_t$. The value of the critical density n_c was found to be of the order of electron density in VO$_2$ in the semiconducting phase, i.e. $n_c \sim n_s \sim 10^{18}$–$10^{19}$ cm^{-3}. Thus, all this suggests that the MIT in VO$_2$ is purely electronic (Mott–Hubbard) transition.

However, classification of transitions as 'Peierls' or 'Mott' is necessarily oversimplified [5]. The Mott transition in vanadium dioxide should be considered as a 'trigger mechanism', which then initiates a structural Peierls-like transition. The latter is accompanied by a symmetry change from monoclinic to tetragonal [2]. Nevertheless, the main driving mechanism for the MIT in VO$_2$ is the transition in the electron subsystem.

Finally, we shall discuss some applied aspects of the above-described results. First, electrical instabilities with the current-controlled NDRs (S-shaped current–voltage characteristic) can be used as switches, memory elements, microsensors, etc. The general trend in the fabrication of such elements are dictated by a natural desire for micro-miniaturization. They are, mostly, low dimensions and, thereby, give the possibility of integration, low power requirements and very fast operation (high speed). Our time delay measurements established, for example, for the VO$_2$-based switches an upper limit of roughly 10^{-9} s. Furthermore, since the transition is driven by electron–electron correlations, the minimum value of the characteristic time is of the order of $\varepsilon \varepsilon_0 \rho$, where $\varepsilon = n^2$ is the high-frequency dielectric constant, $\varepsilon_0 = 8.85 \times 10^{-12}$ F m^{-1} and ρ is the specific resistivity of the material. This value is equal to about 10^{-12} s, i.e. the limit operating frequency would be approximately 1 THz.

Furthermore, three-terminal Si–SiO$_2$–VO$_2$ structures are of special interest. Recently, Zhou *et al* [18] proposed a Mott transition field effect transistor (FET) that was based on hypothetical molecular (Mott insulator) layers. In particular, such exotic materials as K$^+$TCNQ$^-$ (a quasi-monomer organic conductor) or KC$_{60}$ (a doped fullerene) have been proposed. Our version of the Mott-transition FET based on VO$_2$ seems to be more attractive. It demonstrates high speed, low dimensions and (what is more important) it works on the basis of a well studied, reliable material, which has already been tested as a laboratory prototype. In addition, the important merits of vanadium dioxide are that its transition temperature is very close to room temperature and that this material is very thermodynamically stable [13, 14]. This structure also allows its use in opto-electronic devices. The point is that the optical properties of VO$_2$, especially in infrared region, also demonstrate great, sharp and reversible switching due to the MIT [3, 19].

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