

## THE EFFECT OF SEMICONDUCTOR-METAL PHASE TRANSITION ON THE HYDRATE LAYER ON VANADIUM DIOXIDE FILMS

A. V. Zoteev, N. L. Levshin, and S. Yu. Poroikov

The influence of the semiconductor-metal phase transition on the hydration and dehydration processes in polycrystalline vanadium dioxide films has been studied by electrophysical and mass-spectroscopic methods. An enhanced desorption capacity and accelerated adsorption-desorption processes were observed in the temperature region corresponding to the phase transition and also in the vanadium dioxide metal phase.

The adsorptive and electrophysical properties of real surfaces of oxide semiconductors are largely determined by the state of the hydrate overlayer, which comprises hydroxyl OH groups and also water molecules firmly bound by coordinate  $((\text{H}_2\text{O})_c)$  and weaker hydrogen  $((\text{H}_2\text{O})_h)$  bonds [1]. Changes in the concentration of OH groups and  $(\text{H}_2\text{O})_c$  molecules at the surface are responsible for the variation of the electrophysical parameters of the surface, its charge  $\Delta Q_s$ , and the surface conductivity. The  $(\text{H}_2\text{O})_h$  molecules do not practically affect these parameters. The effect of heat treatment and radiation treatment of oxides in vacuum on the composition of the hydrate overlayer has been studied in detail in the literature [1]. Yet, as far as we know, no data have been reported on the influence of a phase transition on the extent of surface hydration. It is particularly urgent to study these processes in view of our finding [2] that adsorption of the  $\text{H}_2\text{O}$  vapor affects the temperature  $T_c$  of the semiconductor-metal phase transition (SMPT) in  $\text{VO}_2$  films, when their resistance  $R$  decreases by four orders of magnitude at  $T_c = 340$  K (Fig. 1, curve 1).

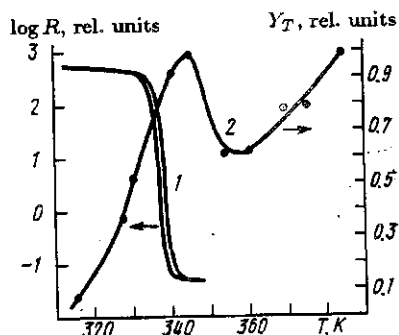


Fig. 1

Resistance of the  $\text{VO}_2$  film (1) and heat desorption yield for  $\text{H}_2\text{O}$  molecules (2) as functions of temperature.

In the present work we have studied the dehydration of  $\text{VO}_2$  films in the 300-385 K temperature interval, which includes the SMPT region, by mass spectroscopy. The specimens were heated in steps at 15 K intervals and the time of film temperature stabilization at each step was 30 min. The desorption products were analyzed in an oil-free  $10^{-6}$  Torr vacuum using an MKh-7301 monopole mass spectrometer.

Changes of the resistance  $\Delta R$  and the charge  $\Delta Q_s$  of the film surface were used as a source of information about the state of the hydrate layer following  $\text{H}_2\text{O}$  adsorption and heat treatment in vacuum. These quantities were always measured after the film was cooled to  $T_0 = 298$  K, when vanadium dioxide is in the semiconducting phase. The measurements were performed in  $\sim 10^{-4}$  Torr vacuum or in a water or oxygen atmosphere. We could not measure the full curve of the field effect, that is of the surface charge  $\Delta Q_s$ , as

a function of the surface potential  $Y_s$ , because of the high density of surface states. To estimate  $\Delta Q_s$  and find the reference ratio between the variations of  $\Delta Q_s$  and  $\Delta R$ , we studied the mobility of the field effect  $\partial\sigma_s/\partial\Delta Q_{\text{ind}}$ , where  $\sigma_s$  is the surface conductivity and  $\Delta Q_{\text{ind}}$  is the charge induced at the surface by the field effect [3]. It was found that in the range of  $Y_s$  variation studied, there is a practically linear dependence of  $\Delta R$  on  $\Delta Q_s$ . The sign of the change of the specimen resistance upon switching on and off the direct electric field indicated that the specimens, which had an  $n$ -type cubic conductance, were covered with a layer having an inverse  $p$ -type conductance.

The specimens were polycrystalline vanadium dioxide films about  $0.3 \mu\text{m}$  thick on sapphire substrates. Electron microscopy revealed that the crystallite size did not exceed  $1 \mu\text{m}$ . There were a small number of pores in the films about  $50 \text{ nm}$  in diameter. Aluminum contacts were deposited on the specimens in order to measure  $\Delta R$  and  $\Delta Q_s$ . An insulating interlayer of mica  $10 \mu\text{m}$  thick was placed between the pressure-loaded electrode and the film in the field effect cell.

As the  $\text{VO}_2$  films were heated in vacuum at  $T > T_c$ , a noticeable desorption of  $\text{H}_2\text{O}$ ,  $\text{CO}$ ,  $\text{CO}_2$ , and  $\text{O}_2$  was observed. In this paper we will only analyze the  $Y_T(T)$  desorption spectra of  $\text{H}_2\text{O}$  molecules. One can see from Fig. 1 (curve 2) that a characteristic feature of the heat desorption curve in the chosen film heating conditions is the presence of a maximum of water desorption in the temperature range close to that of the semiconductor-metal phase transition. This was due to the fact that desorption involves not only water molecules that have been adsorbed on the specimen surface but also water molecules diffused from the film bulk. The crystal lattice undergoes reconstruction during the SMPT which sharply increases the diffusion rate in this temperature interval. Indeed, the desorption maximum broadens as the heating rate  $T(t)$  increases, and it disappears completely with the onset of rapid linear heating regime.

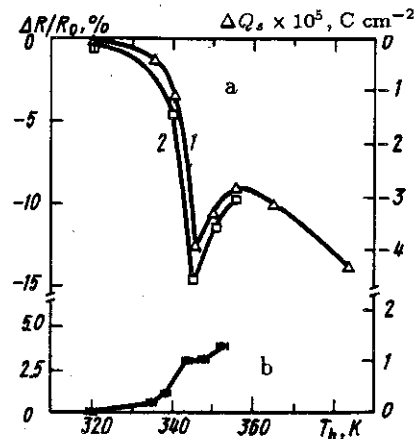


Fig. 2

(a) Relative resistance  $\Delta R/R_0$  and surface charge  $\Delta Q_s$  (at  $T_0 = 298 \text{ K}$ ) of the  $\text{VO}_2$  film versus the temperature of preliminary heating of specimen in vacuum,  $T_h$ . The time of heating is 20 min (1) and 45 min (2). (b)  $\Delta R/R_0$  and  $\Delta Q_s$  versus  $T_h$  following adsorption of  $\text{H}_2\text{O}$ . Water vapor pressure  $p = 2 \text{ Torr}$ .  $T_0 = 298 \text{ K}$ . Exposure to water vapor is 15 min.

To elucidate the mechanism of dehydration in the temperature region studied, we first held the specimen at each heating temperature (Fig. 2 a), then cooled it to  $T_0 = 298 \text{ K}$  and measured the relative resistance of the film,  $\Delta R/R_0$ , where  $R_0$  is the film resistance at  $T_0 = 298 \text{ K}$  prior to its heat treatments in vacuum. Figure 2 a shows that the film resistance sharply drops (the conductivity  $\sigma_s$  grows) in the region of  $T_h$  from 320 to 345 K, passes through a minimum at  $T_h \sim T_c$ , then starts growing. The quantity  $\Delta Q_s$ , linearly related to  $\Delta R$ , changes in a similar way. The temperature region of the  $\Delta R(T_h)/R_0$  and  $\Delta Q_s(T_h)$  minima coincides with the maximum of heat desorption  $Y_T(T)$  of water molecules (see Fig. 1). The presence of extrema suggests that there might be two competing processes under way in the SMPT region. The decreasing  $\Delta R/R_0$  and  $\Delta Q_s$  reflect the removal of donor processes from the surface. It is well known that of the three components of the hydrate layer only water molecules bound by the coordinate bonds ( $\text{H}_2\text{O}$ )<sub>c</sub> can be responsible for the positive surface charging during adsorption and negative charging during desorption. This is confirmed

in numerous experiments with Ge and Si single crystals, and also with various oxides [3]. The negative charging during adsorption and the positive charging during desorption might be due to the dehydroxylation of the surface (by desorption of OH groups), which is always accompanied by a reconstruction of the surface. Dehydroxylation on the outer surface of oxides occurs at higher temperatures (much higher than  $T_c$ ) [1]. However, in fine pores the interactions between the OH groups yield  $H_2O$  molecules that diffuse toward the surface. This process can be quite active in the  $T \sim T_c$  region, where the entire structure of the film undergoes alteration. It is possible that the ascending branch in Fig. 2 a in the SMPT region is related to this particular process.

Note that the slope of the  $\Delta R(T_h)/R_0$  curve in the  $T < 340$  K temperature region is steeper than the slope of the  $Y_T(T)$  curve. The quantity  $Y_T$  includes the desorption of not only  $(H_2O)_c$  molecules responsible for the charging but also of  $(H_2O)_h$  molecules, which exert no effect on  $\Delta Q_s$  and consequently on  $R$ . The width of the  $Y_T(T)$  and  $\Delta R(T_h)/R_0$  maxima determined by mass spectrometric and electrophysical methods is about 20 K, which is much wider than the SMPT region ( $\sim 3$  K) for these specimens (see Fig. 1, curve 1). This is explained by the high defect concentration of the near-surface layer. A similar conclusion is suggested by data obtained by the methods of light scattering by surface irregularities [4] and Raman scattering of light [5], which detect the formation of a new phase 10–15 K prior to the beginning of the SMPT in  $VO_2$ .

Now let us consider the reverse process: water vapor adsorption ( $p = 2$  Torr) at  $T_0 = 298$  K, when  $VO_2$  is in the semiconducting phase. The adsorption caused growth of the film resistance. The  $\Delta R(T_h)/R_0$  curve plotted in the water vapor atmosphere (Fig. 2 b) shows a break at the same temperatures at which there is a maximum on the curves of Fig. 2 a. This demonstrates the effect of the SMPT on the adsorption-desorption properties of vanadium dioxide. Adsorption of water molecules at room temperature fully restored the film resistance within 15 h. Such a prolonged time directly indicates that the slow processes of diffusion and hydroxylation do take place in the film bulk.

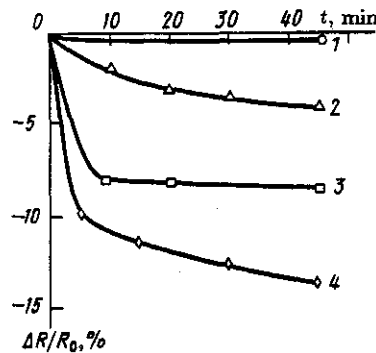


Fig. 3

Dependence of the relative resistance  $\Delta R/R_0$  of the  $VO_2$  film on the time of heating of the film in vacuum. The temperature of heating  $T$  was 318 K (1), 338 K (2), 343 K ( $\sim T_c$ ) (3), and 353 K (4).

Additional information on the mechanism of the adsorption-desorption processes was provided by a study of the kinetic curves. It is evident from Fig. 3 that the relative resistance  $\Delta R/R_0$  of the  $VO_2$  film in the semiconducting phase ( $T_0 = 298$  K) depends on the time and temperature of preliminary heating of the specimen in vacuum. At  $T_h < T_c$  (semiconducting phase) the resistance was declining for several hours. An elevation of the temperature of heat treatment in vacuum to  $T_h \sim T_c$  (curve 3) and to  $T_h > T_c$  (metal phase, curve 4) brought about a considerable increase in the rate of the  $\Delta R(t)/R_0$  variation in the initial stage of desorption ( $\sim 10$  min). The prolonged tails of curves 2 and 4 support the above-mentioned suggestion about a contribution of the slow stages of dehydroxylation in pores with subsequent molecular diffusion from the film bulk.

As shown in Fig. 4 a, the changes in  $\Delta R/R_0$  induced by the water vapor adsorption in the  $VO_2$  film at the semiconducting phase sharply grow at the initial stage as the temperature of specimen heating in vacuum ( $T_h$ ) increases. At  $T_h \geq T_c$  the kinetic curves show a prolonged tail of  $\Delta R/R_0$  variation, which is in

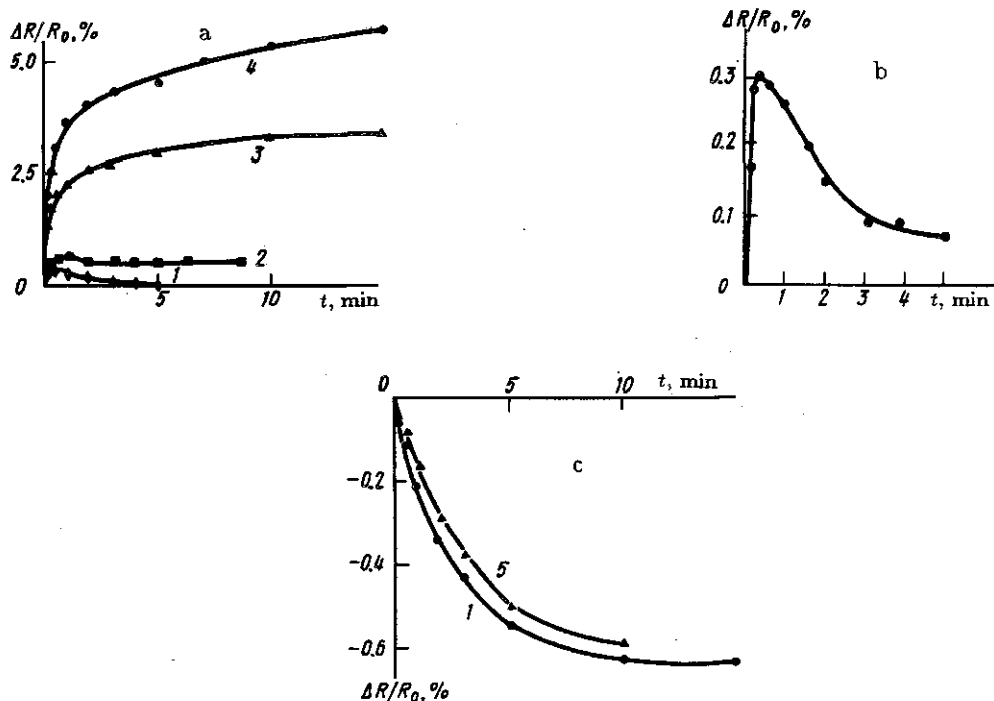


Fig. 4

Kinetics of the variation of the relative resistance  $\Delta R/R_0$  of the  $\text{VO}_2$  film following adsorption of water molecules (a, b) and oxygen (c).  $T_0 = 298$  K, the adsorbate pressure  $p = 2$  Torr. The temperature of preliminary heating  $T_h$  is 298 K (1), 333 K (2), 342 K (3), 380 K (4), and 360 K (5). Figure 4 b is a larger-scale representation of curve 1 from Fig. 4 a.

agreement with similar changes in  $\Delta R/R_0$  during the dehydration (see Fig. 3).

Adsorption of  $\text{H}_2\text{O}$  molecules onto the  $\text{VO}_2$  film that has undergone a prolonged pumping out at  $T_0 = 298$  K gives rise to a maximum on the  $\Delta R/R_0(t)$  curve. A larger-scale representation of this portion of the curve is given in Fig. 4 b. It has been demonstrated in [6] that the maxima on the kinetic curves of semiconductor surface charging during adsorption are results of two processes: (a) production of new adsorption surface states and (b) recharging of the earlier (prior to adsorption) "prehistory" states. Preliminary heat treatment of the specimens in vacuum at  $T_h > 330$  K, which reduced the concentration of the "prehistory" states (coordinately bound molecules  $(\text{H}_2\text{O})_c$  [3]), led to the disappearance of maxima on the kinetic curves (see Fig. 4 a).

For comparison we have studied the effect of oxygen adsorption on the  $\text{VO}_2$  film resistance at the same temperature  $T_0 = 298$  K. One can see from Fig. 4 c that the sign of the surface charge upon adsorption of  $\text{O}_2$  acceptor molecules is opposite to that following the adsorption of  $\text{H}_2\text{O}$  donor molecules, and there is practically no effect of specimen heating at  $T_h \geq T_c$  on the  $\Delta R/R_0$  variation of the film in the semiconducting phase.

The results described above suggest the conclusion that the process of vanadium dioxide dehydration is more active if the vacuum treatment of the film is performed at temperatures of the SMPT range and higher when the specimen is in the metal phase. The latter case is associated with an increase in the amplitude of atomic oscillations in the metal phase [7]. This is also consistent with the findings of earlier studies, which demonstrated that the high-temperature phase of  $\text{VO}_2$  is less resistant to the UV irradiation [8], electron bombardment [9, 10] and ion implantation [11].

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Department of General Physics  
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