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Influence of doping on the properties of vanadium oxide gel films

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Abstract

The effect of doping with H and W on the properties of V_2O_5 and VO_2 derived from V_2O_5 gel has been studied. It is shown that the treatment of V_2O_5 in low-temperature RF hydrogen plasma for 1–10 min leads to either hydration of vanadium pentoxide or its reduction (depending on the treatment conditions) to lower vanadium oxides. For some samples, which are subject to plasma treatment in the discharge active zone, a non-ordinary temperature dependence of resistance, with a maximum at $T \sim 100$ K, is observed. For W-doped VO_2 films, it is shown that substitution of V^{4+} with W^{6+} results in a decrease of the temperature of the metal–insulator transition. Also, it has been shown that the doping of initial films with ~ 3 at.% of W reduces the statistical scatter in the threshold parameters of the switching devices with S-shaped I – V characteristics on the basis of V_2O_5 gel films.

Vanadium oxides are of interest due to metal–insulator transitions (MIT) occurring in many of them at different temperatures [1]. Doping with various elements allows a controllable change of the properties of these materials and the parameters of their phase transitions (transition temperature T_i , hysteresis loop width, etc). These investigations are of importance both for a better understanding of the MIT mechanism and for potential applications, since the transition-metal oxides are the very materials which seem to underlie oxide electronics [2]. In the present work we report on the modification of the electrical properties of hydrated vanadium pentoxide under the action of hydrogen RF plasma treatment, vacuum annealing and doping with tungsten.

Initial film samples were prepared by the sol–gel method. This method is currently considered as a novel and efficient technique to prepare thin films of diverse materials, most of all oxides. In this process, thin films of metal oxides can be deposited directly on the immersed substrate or by spin-coating [3–6]. Among other advantages of this method one can point out that it is easy to apply to various kinds of substrates with a large surface area and complex surface shape [3]. Also, an essential merit of the sol–gel method is the ease

of doping—merely by adding corresponding quantities of a certain composition to the prepared sol.

Vanadium pentoxide gel solution was prepared by the quenching method [3]. Tungsten-doped gels were obtained by adding WO_3 powder directly to the vanadium pentoxide melt [4]. It had been found experimentally that the dissolution limit of WO_3 in V_2O_5 melt corresponded to 12 at.% of tungsten. In order to deposit a film, a few millilitres of the gel solution were placed onto a substrate and excess solvent was allowed to evaporate at room temperature for 24 h. As a result, yellowish-brown xerogel films were prepared with a typical thickness $d \sim 1$ – $5 \mu\text{m}$. These dried-in-air films represented x-ray amorphous $V_2O_5 \times nH_2O$ with a layered structure [5].

The X-ray diffraction pattern of the initial V_2O_5 -gel film is presented in figure 1; the interlayer spacing is 11.5 Å (measured from the (001) diffraction peak at $s = 0.55 \text{ \AA}^{-1}$), which corresponds to the water content $n = 1.6$ – 1.8 [3, 5]. Water can be removed upon heating to $n = 0.1$ – 0 at $T = 210$ – 270°C . Amorphous V_2O_5 is obtained at this temperature, and crystallization into orthorhombic V_2O_5 occurs around 350°C [3]. Vanadium dioxide can be easily prepared by a thermal treatment at $T \sim 500^\circ\text{C}$ in vacuum

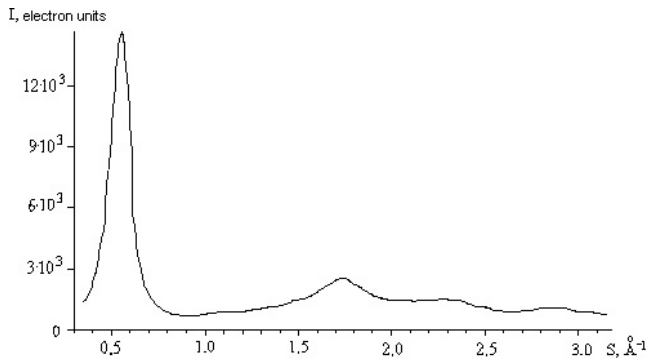


Figure 1. X-ray intensity as a function of diffraction vector $s = 4\pi \sin \theta / \lambda$ (where θ is the diffraction angle and $\lambda = 0.7107 \text{ \AA}$ —Mo—K α radiation) for $\text{V}_2\text{O}_5 \times n\text{H}_2\text{O}$ film.

or a reducing atmosphere [4–6]. The formation of VO_2 rather than other lower vanadium oxides is accounted for by its thermodynamic properties [7], and preparation of other vanadium oxides in a thin film form is very difficult due to the narrowness of the stability range of any oxide [3, 7].

The possibility of doping with hydrogen has been studied with samples of amorphous V_2O_5 , obtained by the thermal treatment of an initial $\text{V}_2\text{O}_5 \times n\text{H}_2\text{O}$ film in air at $T = 250^\circ\text{C}$. Plasma treatment has been performed in an RF (2.45 GHz) hydrogen reactor with remote plasma [8]. Design features of the reactor exclude the sample heating, permitting, however, its contact with low-energy H^+ ions and atomic hydrogen.

First, we present the experimental results obtained at various pressures p (10–100 Pa) in the reactor, time t of treatment (20 s to 10 min) and the distance l of the treated sample from the discharge active zone (0–10 cm). At $t < 1$ min and $l = 5$ –10 cm, an effective hydrogen insertion has been observed: the appearance of an internal electrochromic effect [3] reveals the hydrogen intercalation into V_2O_5 . This internal electrochromic effect is associated with hydrogen redistribution inside the V_2O_5 gel film; that is, the process of plasma treatment results in formation of polyvanadic acid $\text{H}_x\text{V}_2\text{O}_5 \times n\text{H}_2\text{O}$ with $x = 0.3$ –0.4 [3]. It is pertinent to mention here that the insertion of hydrogen into vanadium oxides with formation of vanadium oxide bronzes is not an emergent phenomenon: it is observed during electro- and photochromism [9, 10], and even merely by means of immersion of a vanadium oxide film into a hydrogen-containing liquid [11].

Appropos of RF plasma treatment, we encountered the fact that varying the parameters (p , t , l) it was possible to obtain any lower vanadium oxide. As an example, the resistance temperature dependence for one of the samples, presented in figure 2 (curve 1), shows the MIT at $T_t \approx 170$ K which is characteristic of the V_6O_{11} phase of the $\text{V}_n\text{O}_{2n-1}$ series [1].

Moreover, what happens on placing the sample directly into the discharge is remarkable. Curve 2 in figure 2 demonstrates the temperature dependence of resistance for the sample, which is plasma-treated in the centre of the discharge ($l \approx 0$) at $p = 100$ Pa. This result is rather unforeseen: such an $R(T)$ curve with a maximum has never been reported for vanadium oxides heretofore. In the high-temperature region

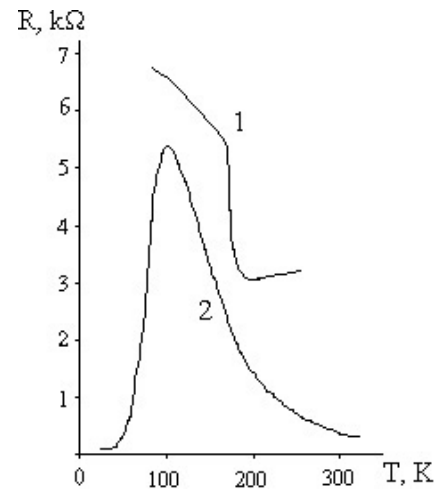


Figure 2. Temperature dependence of resistance (on cooling) of the vanadium oxide samples subject to plasma treatment (1) for $t = 1$ min in the centre of the waveguide ($l = 5$ cm) and (2) for $t = 2$ min directly in the discharge ($l = 0$).

this dependence has a semiconducting character followed by the sharp resistance fall at $T < T_m \approx 100$ K by almost two orders of magnitude, and the specific resistivity at $T = 20$ K has been estimated to be $\rho \approx 0.1 \text{ } \Omega \text{ cm}$ for the film thickness of $5 \text{ } \mu\text{m}$.

The above-described behaviour of the $R(T)$ dependence might be attributed to a re-entrant (or ‘inverse’) MIT. The second high-temperature transition in $(\text{V}_{1-x}\text{Cr}_x)_2\text{O}_3$ (besides the first ‘usual’ MIT at $T_t = 150$ K) [1, 12, 13] is an example of such an inverse MIT: the metallic phase is low temperature and the high-temperature phase is insulating. Another example of inverse MIT is a more spread-out transformation in $\text{NiS}_{2-x}\text{Se}_x$, for which T_t ranges from 30 to 100 K with variation of x . Also, $\text{BaCo}_{0.9}\text{Ni}_{0.1}\text{S}_{2-y}$, europium oxide, CMR manganites and some other materials demonstrate that same behaviour—see the pertinent surveys [1, 12–14] and references therein. However, the experimental curve (2 in figure 2) might also be an indication of superconductivity (SC): a similar dependence of R on T is characteristic of some under- and over-doped HTSC cuprates (such as, for example, $\text{TlCa}_{1-x}\text{Nd}_x\text{Sr}_2\text{CuO}_4$ at $x = 0.75$ [12]).

As regards the phase composition of those samples, treated in low-temperature RF hydrogen plasma, x-ray analysis shows a mixture of lower vanadium oxides, which are difficult to distinguish. Presumably, if we do deal with a vanadium-based SC phase [15, 16], it might be a certain hydrogen bronze $\text{H}_x\text{V}_n\text{O}_{2n-1}$ of a Magneli-phase lower vanadium oxide.

Next, we have doped the vanadium oxide gel with tungsten as described above (see also [4] where the process of doping is described in more detail). The films deposited from such a gel represent the following composition: $\text{V}_{2-y}\text{W}_y\text{O}_{5\pm\delta} \times n\text{H}_2\text{O}$, where y is varied from zero (pure V_2O_5 gel) to 0.12 and $n = 1.6$ –1.8. These films, after vacuum annealing, transform into vanadium dioxide doped with tungsten. Influence of doping on the electrical properties of VO_2 is demonstrated by figure 3. An increase in the W content leads to a decrease in the resistivity of the sample and in a shift of the transition temperature

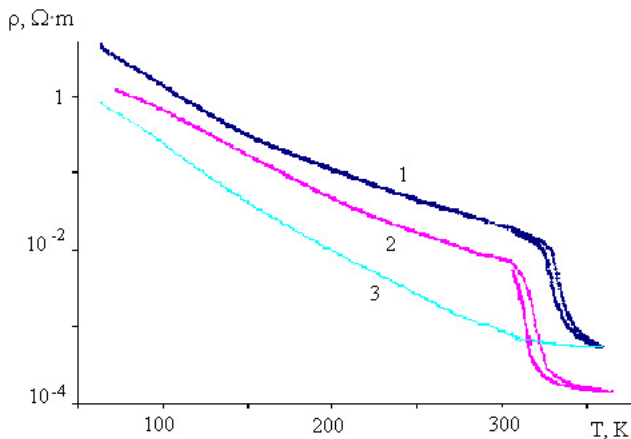


Figure 3. Resistivity versus temperature for vanadium dioxide (1) and for VO_2 doped with 3 at.% (2) and 12 at.% (3) of tungsten. (This figure is in colour only in the electronic version)

T_t towards the low-temperature region. In addition, some modification of the hysteresis loop parameters is observed, as is discussed in the work [4]. At the impurity content of more than 6 at.%, the MIT no longer occurs, though the $R(T)$ dependence remains still semiconducting (figure 3, curve 3). For complete metallization of VO_2 , the concentration of W dopant should be ~ 14 at.% [17].

It is understandable that ‘metallic’ VO_2 (i.e. $\text{V}_{1-x}\text{W}_x\text{O}_2$ with $x = 0.14$ [17] or H_xVO_2 with $x = 0.04$ [11]) could serve merely as a precursor to search for superconductivity [15, 16]. Experience shows that all the known HTSC materials are strongly correlated metals (in normal state) and that they are prone to MIT. The next stage should be to intercalate some additional elements (e.g. hydrogen, alkali or alkali-earth atoms) into this host precursor structure. Light electronegative elements promote an enhancement of the ionicity bond degree [18] and contribute to the softening of the phonon modes, which is important for the appearance of HTSC. The scepticism of the scientific community with regard to the search for new SC materials amid non-Cu-based (particularly V-based) compounds¹ is founded, among other arguments, upon the opinion that ‘binary structures with only two sites per unit cell lack the possibility of being able to substitute and introduce charge carriers without introducing disorder directly into the conduction band, and thus are considered to be less likely candidates for supporting SC than more complex structures’ [15]. However, the ability of vanadium oxides to be substituted (e.g. $\text{V} \rightarrow \text{W}$ or Mo) and intercalated (by alkali and alkaline-earth atoms) simultaneously [20, 21] seems to remove this argument. In addition, according to the authors of [17], the samples of $\text{V}_{1-x}\text{W}_x\text{O}_2$ with x up to 0.14 remain quite ordered with undistorted rutile structure.

Finally, we have studied the switching effect in the MDM structures on the basis of W-doped V_2O_5 gel films. These structures require preliminary electroforming [3] resulting in

¹ Note that a copper-less HTSC material La-O(F)-Fe-As has been discovered recently [19].

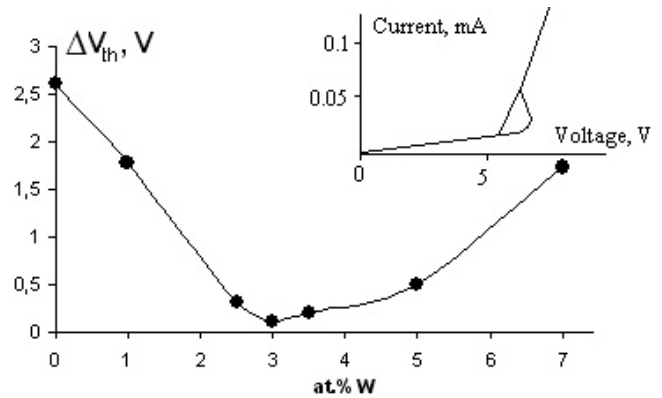


Figure 4. Threshold range (V_{th} scattering) as a function of W admixture percentage. A typical $I-V$ curve of $\text{Au-V}_{2-y}\text{W}_y\text{O}_5 \times n\text{H}_2\text{O-Au}$ sandwich structure with $y = 0.03$ is shown in the inset. Thickness for all the samples is $d \sim 1 \mu\text{m}$ and the mean value of V_{th} is actually independent of W concentration ($\langle V_{th} \rangle = 7.1 \pm 1.5 \text{ V}$ with reliability 0.95).

formation of a conducting channel within the initial dielectric film. The channel consists of vanadium dioxide and switching is associated with the insulator-to-metal transition in VO_2 . As was shown in [3], for the pure (undoped) V_2O_5 gel, the switching parameters vary over a wide range, because the phenomenon of electrical forming is statistical in nature (likewise electrical breakdown), and its statistical character shows itself as a spread in the observed threshold voltages of the ensuing structures.

In this work, we have found that the statistical spread in values of the threshold parameters can be minimized by means of doping (figure 4). Unsophisticated reasoning could account for this result: for pure V_2O_5 gel, electroforming leads to formation of VO_2 with $T_t = 340 \text{ K}$, and each switching event requires heating up and cooling down from room temperature to T_t ; this thermal cycling can modify the peripheral regions of the channel, which leads to the change of the switching threshold voltage. On the other hand, for the samples with a high concentration of W, the MIT is suppressed (see figure 3, curve 3) and switching is degenerated. Between these two outermost points, an optimum should exist. As one can see from figure 4, this optimal value corresponds to 3 at.% of W, i.e. for $\text{V}_{0.97}\text{W}_{0.03}\text{O}_2$ the switching parameters are the most stable. The transition temperature of $\text{V}_{0.97}\text{W}_{0.03}\text{O}_2$ (figure 3, curve 2) is lower than that for pure vanadium dioxide, and hence the magnitude of the aforesaid thermal cycling is decreased, which results in an increase in stability of the switching parameters.

To summarize, it is shown that doping with tungsten and hydrogen affects severely the electrical properties of vanadium oxides. The treatment of V_2O_5 in low-temperature hydrogen plasma leads to either hydration of vanadium pentoxide or its reduction to lower vanadium oxides. Doping of VO_2 with W leads to a decrease of the transition temperature, which is in accordance with the literature data [4, 17] and supports the Mott mechanism of MIT in vanadium dioxide [13, 22]. The introduction of ~ 3 at.% of W reduces the scatter in the threshold voltage of the switching MDM structures on the basis of V_2O_5 gel.

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