Study of the metal-dielectric phase transition of VO$_2$: N film

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Annotation. In our work we studied the magnetic and electrical properties of thin VO$_2$: N films, as well as the technology for producing films from the gas phase by the pyrolysis method. The features of the phase transition in VO$_2$: N films are described, the anomalies found in the curve of the temperature dependence of electrical resistance, as well as the memory phenomenon and kinetics of the phase transition in VO$_2$: N films are explained.

1. Introduction

The physical properties of a substance in a thin-film state can differ significantly from the properties of the same substances in a massive state. The small thickness of the films leads to such phenomena, such as the tunneling effect in metal-insulator-metal (MIS) sandwiches, an increase in electrical resistance and a decrease in the temperature coefficient of electrical resistance due to an increase in surface scattering of carriers, a change in superconducting properties when the thickness of the sample compares with the penetration depth of the magnetic field. The field effect in MIS structures, size effects associated with the fact that the film thickness is comparable with the mean free path or with the length of the de Broglie wave of electrons, and many other effects associated with the thin-film state make them promising in scientific and applied terms. However, to obtain unambiguous results, it is necessary to know the process of film growth, the effect of substrates, and other factors associated with the growth of films.

A variety of structural characteristics of thin films at different stages of condensation and the manifestation of size effects in them are the main reasons for the change in the physical properties of substances in the thin-film state.

Size effects are phenomena consisting in a change in the physical properties of substances with a change in their size, as a result of an increase in the contribution of surface processes compared to bulk ones. The surface contribution is essential for the phase state of small objects and can be taken into account by adding the term corresponding to surface energy to the corresponding thermodynamic (potentials) ratios.

This allows us to describe the change in the films (and small particle powders) of phase transition temperatures and other effects due to the influence of surface energy on the phase and structural state of thin films [1].
Electron-diffraction and x-ray studies of the structure of thin films obtained at room temperature have shown that “directed” phases, in particular high-temperature ones, can often be detected in thin films. These unusual phases are most often formed in the films of those elements that have polymorphic transitions with a change in temperature or pressure. In [2], the appearance of metastable modifications in thin films is associated with a change in the phase equilibrium conditions, which occurs as a result of a change in free energy due to the relatively large surface of the film. If in a massive crystal of two possible modifications under these conditions the equilibrium is phase I, which has less free energy than phase II i.e. $F_1 < F_2$, then for a thin film with allowance for surface energy this inequality may turn out to be the opposite:

$$F_1 + \frac{\sigma_1}{d} > F_2 + \frac{\sigma_2}{d}$$

and therefore in films thick

$$d < d^* = \frac{\sigma_1 - \sigma_2}{F_1 - F_2}$$

phase II should be observed. $d^*$ is the critical thickness (phase transition), upon reaching which the sample should undergo a transition from phase II to phase I, i.e. in films, a transition from a volume-centralized cubic (VCC) to a face-centered cubic (FCC) structure is likely. In addition, the formation of a hexagonal close packing (HCP) structure is also likely instead of a triclin-centrally cubic (TCC) [2].

2. The technology of deposition of films. Research methods

Studies of the growth conditions of thin layers of vanadium dioxide by thermal decomposition of organometallic compounds have shown that, when compounds containing oxygen and any of the elements of group IV are decomposed, films with an admixture of this element can be obtained. In this way, during the thermolysis of tris (tert-buty) vanadium chalcogenides and vanadium alkoxides containing nitrogen, it was possible to precipitate: films of the V–O–N systems [3]. In particular, thermal decomposition of nitrogen-containing alkoxy derivatives of vanadium provides doping of vanadium oxides with nitrogen.

The films were deposited at a temperature of 520 K, followed by annealing at a temperature of 570 K. Polycrystalline plates of glass, corundum, and single-crystal plates of lithium fluoride and magnesium oxide were used as substrates. The nitrogen content in the films was determined by gas chromatography on a “Colour-I04” chromatograph using adsorbent molecular alkoxide Ca-A and helium as a gas carrier. For this purpose, the films were annealed in quartz ampoules at an oxygen pressure of 300 mm Hg and a temperature of 620 K. The accuracy of the determination of nitrogen is 15-20%. The vanadium content in these films was determined by spectrophotometric methods.

The phase composition of the films was studied by X-ray phase analysis on a “Dron-4” X-ray diffractometer using Cu-K radiation.

The temperature dependence of the electrical resistance of the films was measured in direct current by the two-probe method. The contacts to the samples were fixed by applying a conductive adhesive based on polyacrylic resin to the film surface, as well as by vacuum deposition of silver. In measurements of electrical resistance, films 3 mm wide and 3.5 mm long were used. The current-voltage characteristics (CVC) of the films were measured on a two-coordinate potentiometer - the PDS-021 recorder. For this purpose, a reference linear resistor was sequentially included in the circuit containing the power source and the test sample, the voltage of which determined the current strength in the circuit.

When measuring the I–V characteristics, films 1 mm wide and 0.5 mm long were used.

The contacts to the samples were fixed by thermal evaporation of copper through a mask in a vacuum of $10^{-5}$ mm Hg. When applying copper contacts, we were guided by the methods described in [3] with the aim of producing homogeneous copper layers in thickness since this ensures the ohmicity of the contacts and avoids their rectifying actions. They also used silver paste (based on polyacrylic resin) as contacts, after applying which the contacts were annealed to ensure mechanical strength and ohmic resistance. Figure 1 shows the results of testing silver paste for ohmicity.
3. Results and discussion

The metal – insulator phase transition (MIPD) was studied on VO$_2$: N films deposited on various substrates [5–7]. In all cases, qualitatively unambiguous results were obtained. Figure 2 shows the temperature dependences of the resistance of the VO$_2$: 0.20 N film with a thickness of 970 Å on a glass substrate measured at different heating rates. Its peculiarity is a jump in electrical resistance at a temperature of 250 K, an abnormally large temperature hysteresis of electrical resistance, and the non-monotonic nature of electrical resistance if the sample is heated quickly enough. Figure 3 shows the dependences of the width of the temperature hysteresis $\Delta T$ and the width of the additional peak on the heating and cooling rates of the samples. At a heating rate close to 8 deg/min, repeated measurements show not one peak, but several oscillations. When the heating rate is less than 8 deg/min, the extra peak disappears. Upon annealing of films above 600 K, as the nitrogen “burns out”, the jumps in the electrical resistance increase, the hysteresis width decreases, the high temperature anomaly disappears, and the MIPD temperature monotonically tends to 340 K, which is typical for pure VO$_2$ [8].

The basis for explaining the results was the assumption of the decisive role of nitrogen solubility in the dielectric and metallic phases of VO$_2$, and its influence on the nature of the phase transition and its kinetics [9]. Since the unit cell volume of the metal phase in VO$_2$ is larger than the dielectric, it should be expected that the solubility in it will be greater.

In this case, the phase equilibrium during PMFD will be disturbed due to a significant contribution to the thermodynamic potential of configurational entropy. In the limiting case of the complete solubility of nitrogen in the metal phase and its insolubility in the dielectric phase, provided that the nitrogen is chemically inert with respect to VO$_2$, an estimate can be obtained for the temperature of the MIPD. The entropy increment in the VO$_2$ metal phase due to the solubility of nitrogen is given by the Boltzmann formula

$$S = k \ln P$$  \hspace{1cm} (1)

where $P$ is the number of ways of placing nitrogen atoms in the matrix $P = \frac{(N+n)!}{N!n!}$

$n/N$ - is a specific nitrogen content.

In the Stirling approximation, we have:

$$S = k[(N + n)\ln(N + n) - N\ln N]$$
Figure 2. Temperature dependences of the electrical resistance of VO$_2$ films: 0.20 N, measured at different heating rates of samples: 1-21 deg / min: 30 deg / min 75 deg / min.

Figure 3. Dependence of the temperature hysteresis of the MIPD $\Delta T$ and the width of the additional peak $\delta T$ on the heating and cooling rates of the samples.

The dissolution of nitrogen disrupts the phase equilibrium during the transition and shifts the equilibrium transition temperature $T^o_k$ and changes the chemical potentials of the phases:

$$\Delta T^o_k = \frac{\partial F}{\partial N} = -\frac{\partial S_T}{\partial N} = \frac{n}{N} kT + M_{az}$$

where

$$M_{az} = \frac{\partial F}{\partial N}$$

(since $n<<N$)

because the

$$\frac{\partial M}{\partial T} = \frac{\partial}{\partial T} \left( \frac{\partial F}{\partial N} \right) = -\frac{\partial S}{\partial N}$$

where $S$ is the entropy per molecule, then

$$\Delta T^o_k (S_1 - S_2) = \frac{n}{N} RT$$

as $S_2 - S_1 = Q/T^0_K$ where $Q$ is the latent phase heat transition, we finally get

$$T_K = T^0_K - \frac{n}{N Q} T^0_K$$

For the considered case $n/N = 0.2$, we have $T_K = -280$ K, which is close to the experimentally observed temperature of the MIPD.
Since the process of dissolution of nitrogen during MIPD occurs at a finite rate limited by diffusion, the nature of the phase transition will depend on the rate of heating and cooling of the samples [10]. The critical size of the nucleus of the high-temperature phase in the low-temperature phase in the hysteresis region is determined by the competition between the bulk and surface energies and can be represented as

\[ r_K^* = \frac{2\sigma T_K}{Q(T-T_K)} \]  

(7)

where \( \sigma \) is the density of surface energy.

With constant \( \sigma \), nuclei larger than \( r_K^* \) continue to grow irreversibly, while nuclei of smaller sizes collapse. However, at a high nucleation growth rate, initiated, first of all, by the heating rate of the sample, due to the finite dissolution rate of nitrogen, the surface energy density can also increase, which ultimately will cause an increase in \( \sigma \) and the reverse collapse process. However, at a high nucleation growth rate, initiated, first of all, by the heating rate of the sample, due to the finite dissolution rate of nitrogen, the surface energy density can also increase, which ultimately will cause an increase in \( \sigma \) and the reverse collapse process. At a low speed, large fluctuations are experienced by such fluctuations; at a low speed, a wider circle is involved in this process. Qualitatively, this is consistent with the results in figure 2. The above means that the development of nuclei is a thermodynamically nonequilibrium process, and the initiation of their growth under conditions close to adiabatic at a certain stage can cause a decrease in temperature. This determines the monotonicity of the change in electrical resistance near the MIPD. According to this assumption, a similar mechanism should always manifest itself during martensitic transformations in the presence of relaxing impurities.

Observation of this phenomenon is most convenient for phase transitions with a change in electrical resistance, since the latter, being a structurally sensitive value, allows one to reveal the kinetics of the phase transition. As a result of studies of the nonlinear resistive properties of VO\(_2\): 0.20 N solid solution films, a memory effect was discovered. Whereas for VO\(_2\) films and other compounds with MIPD, the region of negative resistance on the current-voltage characteristic (I–V) is unstable and switching occurs in \( 10^{-4} - 10^{-3} \) sec In these samples it is highly conductive and the low-conductivity state, differing in electrical resistance by almost two orders of magnitude, can be maintained at a voltage below the threshold. Memory exists in a wide temperature region below the temperature of the MIPD [11]. The existence of memory in these films can be explained on the basis of the following considerations. The development of the channel of the conducting phase during switching is a nonequilibrium process, and the phenomena at the channel boundary are similar to those that arise during the growth of the nuclei of the conducting phase during MIPD. Since, as a rule, switching occurs rather quickly, the diffusion of nitrogen across the boundary does not have time to complete, and this leads to effective inhibition of the boundary. In other words, due to the large dynamic temperature hysteresis, the nonequilibrium state on the negative I – V characteristic branch with increasing voltage always corresponds to the equilibrium state on the positive I – V characteristic branch with decreasing voltage, which leads to stabilization of the high-temperature phase.

4. Conclusions

By the method of thermolysis of nitrogen-containing alkoxy derivatives of vanadium, films of vanadium dioxide with a nitrogen content of 0.1 - 0.2 per formula unit VO\(_2\) on various substrates were obtained.

A jump in electrical resistance in the region of 280 K and an abnormally large temperature hysteresis of electrical resistance were detected.

The phenomenon of memory on the current-voltage characteristic in the studied films was discovered. It is shown that memory is a consequence of a jump in electrical resistance and its temperature hysteresis.

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