Martensitic transformations in VO2 films

X O Urinov¹, X A Jumanov¹, A K Amonov¹, A M Xidirov¹, J R Kilichov and J X Nurmurodi²

¹Samarkand branch of Tashkent University of information technologies named after Mukhammad al-Khwarizmi, 47A Sh.Mirzo Street, Samarkand, 140100, Uzbekistan

e-mail: adkham1972@gmail.com

Abstract. Martensitic transformation is considered to be non-diffusive since the atoms in the transition are moved to a distance of the order of interatomic, and neighboring atoms in the initial phase remain adjacent and in the new one, only their position changes. In this paper, for the first time, an experimental study of the phase transition metal-dielectric (FPMD) in thin films of vanadium dioxide is accompanied by a structural transition of martensitic type, so this material is a convenient model object that allows you to clearly identify both the processes of defect formation and their influence on its physical properties in the vicinity of the phase transition point. The obtained results are naturally associated with the effect of adhesion and epitaxy on the phase transition, which can be reduced to the contribution to the energy balance of the component σ/d, where σ is the density of the surface energy; d is the film thickness. Physically, this may mean that since the growth of films occurs at a temperature above the FPMD temperature, the orientation of the crystal axes of the high-temperature tetragonal phase is stabilized by epitaxial forces from the substrate side, and this makes it difficult to reconstruct the crystal structure during the phase transition. Phase stabilization in thin layers due to surface effects is a common phenomenon in the physics of thin films.

Introduction

Martensitic transformation is a phase transition of the first kind, occurring by the origin and growth of a new phase, fully or partially coherent with the original. Metaphase boundaries are sources of internal stresses caused by the difference between the specific volumes of the initial and new phases. The products of martensitic transformation are polycrystalline phases, which are packages of plane-parallel layers – elastic domains [1]. Elastic domains can serve as a variety of crystalline phases and orientational variants of the same phase. Martensitic transformation is considered to be non-diffusive since the atoms in the transition are moved to a distance of the order of interatomic, and neighboring atoms in the initial phase remain adjacent and in the new one, only their position changes. Martensitic transformations, under which, at the present time, I understand the whole class of phase transitions, got its name from the martensite – a very hard phase a kind of leaf shaped, formed, in the hardening by rapid cooling from the austenitic state of the alloy based on Fe-C. Under these conditions, cooling eutectoid diffusion and the release of carbon from solid solution becomes impossible. Under these conditions, the thermodynamic phase is more stable than austenite and can be obtained by the shear movement of atoms, in which a solid solution of carbon in iron with a face-centered cubic lattice is converted into a solid solution of carbon in iron with a volume-centered lattice – martensite.

In body-centred cubic lattice the iron dissolved is not more than 0.02 %; in the martensite, the carbon concentration is the same as in austenite, i.e. it can reach 1.7 %. But at the same time the lattice, remaining volume-centered, cubic lattice turns into a tetragonal one with an ordered arrangement of carbon atoms.

The transformation of austenite into martensite is characterized by an increase in the specific volume of steel by 1 % (it is the more carbon in steel). Therefore, as already mentioned, the transformation is accompanied by a sharp increase in the elastic deformation of the lattice; the accumulation of elastic energy prevents the transformation and under certain conditions may not allow it to complete [2]. To
continue the transformation in this case, it is necessary to create an additional driving force by further lowering the temperature or applying a favorable sign of external deformation.

The effect of the subsequent reduction of the tetragonalicity of irradiated martensite as a result of short-term cooling in liquid nitrogen or rapid heating to room temperature was unexpected. Lowering tetragonality in this case happens abruptly and is a kind of phase transition of martensite. Such uncharacteristic non-irradiated martensite change at low temperature parameters of the lattice is not associated with since these transitions do not require carbon diffusion over long distances, they occur within the unit cell. The presence in the martensite lattice of point defects created by irradiation stimulates the transition of carbon atoms from one lattice position to another, energetically more favorable at these temperatures. The validity of this statement is evidenced by the results of the experiment, showing the chemical stability of irradiated martensite compared with non-irradiated (under the same conditions), since radiation defects prevent the diffusion of carbon atoms over long distances and thereby prevent the formation of carbides.

In this respect, thin films are a kind of analogue of irradiated martensite, since they are inherent in structural imperfections associated with structural imperfection of the substrate with a mismatch of the parameters of the film lattice and the substrate, etc., as a result of which the compound in the thin-film and massive States may have different properties under the same conditions. The above-mentioned defects can serve as places of localization of relaxing impurities. Good adhesion of films on substrates prevents the destruction of crystals and the growth of defects in the martensitic transition. Therefore, in addition to the mechanical strength of the film, they are stable in physical and chemical terms.

The phase transition metal-dielectric (PTMD) in thin films of vanadium dioxide is accompanied by a structural transition of martensitic type, so this material is a convenient model object, which allows to clearly identify both the processes of defect formation and their influence on its physical properties in the vicinity of the phase transition point\[3,4,5\].

2. Experimental technique and sample preparation

One of the most important characteristics of \(V_02\) is the temperature of PTMD \(T_k=340\) K. As noted in the review, the all-round pressure leads to an increase in TC, cationic substitution can lead to both an increase and a decrease in it depending on the impurity, etc.

Here are the results of the study of the effect of the substrate and film thickness on the temperature of PTMD in \(V_02\) [6].

\(V_02\) films were obtained by pyrolysis of vanadium acetylacetonate, the low deposition temperature of which allowed to obtain films on various substrates. Mica, Sitall, corundum (\(\text{Al}_2\text{O}_3\)), lithium fluoride (LiF) and magnesium oxide (MgO) Plates were used as a substrate. Upon receipt of the films were kept constant optimal substrate temperature 360 K and pressure of oxygen because of the synthesis of 50-60 mm of mercury the deposition Rate of films is 0.1 \(\mu\text{m/MIN}\). The contacts were made by applying and then firing silver paste, and the distance between the contacts was 5 mm.

The result of this work was to establish the fact that the temperature of PTMD TC in \(V_02\) films is always lower than for massive material, table 1. For rice. 1 the results of measurements of the temperature dependence of electrical resistance of films with a thickness of 0.47-0.51 microns on different substrates are shown. Here, for comparison, the temperature dependence of the resistivity of a massive crystal is given.

The temperature of the PTMD on the same substrates is monotonically decreasing with decreasing film thickness, So the temperature of the PTMD films on mica and magnesium oxide with a thickness of 0.02 and 0.01 \(\mu\text{m}\), respectively, is 317±1 and 316±1 In Fig. 2 shows the thickness dependence of the temperature of PTMD films on a magnesium oxide substrate.
The obtained results are naturally associated with the effect of adhesion and epitaxy on the phase transition, which can be reduced to the contribution to the energy balance of the component \( \sigma/d \), where \( \sigma \) is the density of the surface energy; \( d \) is the film thickness. Physically, this may mean that since the growth of films occurs at a temperature above the PTMD temperature, the orientation of the crystal axes of the high-temperature tetragonal phase is stabilized by epitaxial forces from the substrate side, and this makes it difficult to reconstruct the crystal structure during the phase transition. Phase stabilization in thin layers due to surface effects is a common phenomenon in thin film physics [7,8].

### Figure 1
Temperature dependence of the resistivity of the films VO₂ of thickness 0.47-0.51 microns on various substrates: 1-MgO; 2-LiF; 3-Al₂O₃; 4 - sital; 5-data for the solid crystal [3].

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### Figure 2
The temperature PTMD films VO₂ on a substrate of magnesium oxide.

### 3. Results and discussion
Consider the phenomenological state of the film and the massive crystal at the phase transition [7]:

\[
F_1(T_k) = F_2(T_k), \quad F_1^o(T_k^o) = F_2^o(T_k^o),
\]

where \( F \) is the density of free energy; index “o” characterizes the properties of a massive crystal; indices ”1” and ”2” respectively refer to the metal and dielectric phases. The equations of state of the film and
the massive crystal can be written in the form

\[ U_1 + \frac{\sigma_{1}}{d} - T_k S_1 = U_2 + \frac{\sigma_{2}}{d} - T_k S_2 \]  

(2)  

\[ U_1 - T_k^0 S_1 = U_2 - T_k^0 S_2 \]  

(3)  

where \( U \) – the internal energy density; \( S \) - entropy.

Obviously, the form of writing the phase equilibrium equation (I) imposes a limit on the lower limit of film thickness; this means that the contribution of surface energy to the total free energy should be small and should not change the thermodynamic properties of the film material. The limitation on the applicability of the model should be sought from the comparison of experimental results with the calculated data. From equations (I) and (3) it is easy to obtain an expression for the phase transition temperature of the film:

\[ T_k = T_k^0 - \frac{\Delta \sigma T_k^0}{dQ} \]  

(4)  

where \( \Delta \sigma = \sigma_2 - \sigma_1 \) is the difference between the surface energy densities of both phases;

\[ Q = \frac{(S_2 - S_1)}{T_k^0} \]  

(5)  

latent heat of phase transition.

As shown in Fig. 2 the experimental results are well described by the expression (3) starting with a film thickness of 3 µm. From the \( T_k (d/d) \) graph in particular, it is possible to estimate the difference between the surface energy densities of both phases. Using the value for the transition heat in VO\(_2\) \( Q=1.02 \text{ kcal/mol} \) [9], we obtain \( \Delta \sigma = 2 \times 10^7 \text{erg/cm}^2 \) for the case of films on a magnesium oxide substrate.

| Substrate    | \( T_k, \text{K} \) | Film thickness, µm |
|--------------|---------------------|--------------------|
| MgO          | 320 ± 1             | 0.51               |
| LiF          | 323 ± 1             | 0.50               |
| Al\(_2\)O\(_3\) | 325 ± 1             | 0.50               |
| sitall       | 333 ± 1             | 0.47               |
| Mica         | 333 ± 1             | 0.49               |
| Massive crystal | 340 ± 1           | –                  |

Thus, the martensitic mechanism of transformation into steel plays an important role not only in the practice of metallurgy, but also in the fields of science and technology. In recent years, the metal-dielectric phase transition in semiconductor oxides of doped impurities of various kinds has been interpreted often involving the martensitic transition mechanism.

**Conclusion**

In this paper, an experimental study of FPMD in VO\(_2\) films of different thicknesses on different substrates was carried out for the first time. Studies of PTMD in VO\(_2\) films of different thicknesses on different substrates. It is shown that the decrease in the transition temperature in the films is due to surface phenomena at the film-substrate interface.

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