Features of vanadium dioxide films deposition by reactive magnetron sputtering

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Abstract. In this work, influence of substrate material and technological process parameters on the stoichiometric composition, crystal structure and phase transition character in vanadium oxide films deposited by the magnetron sputtering method is investigated.

1. Introduction
Vanadium oxide films provide unique opportunity for their application in thin-film interferometers [1], IR radiation modulators, tunable microwave keys and other devices [2] due to semiconductor properties. The operation principle of these devices is related with the metal-semiconductor phase transition, which takes place in vanadium oxide films at different temperatures. Films are actively used in linear polarizers, wave THz modulators and variable THz attenuators. Nanofilms (V$_2$O$_3$, VO$_2$ and V$_2$O$_5$) can be used as biosensors attributable to the significant inhibiting ability of VO$_x$.
Vanadium dioxide is particularly interested since the phase transition temperature in VO$_2$ films, in contradistinction to other modifications of vanadium oxide, is 68 °C (340 K), which is as close to room temperature as possible. However, the synthesis of this oxide is possible in a narrow stoichiometric range, which is determined by the formula VO$_{2.δ}$ (δ < 0.006). To reduce this temperature, vanadium oxide is doped with a donor impurity of vanadium W [3], niobium Nb and molybdenum Mo [4].

Most of the articles are devoted to the study of the microstructure, electrical and optical properties of VO$_2$ films deposited on sapphire substrates by the pulsed laser ablation. Well-oriented VO$_2$ films were obtained on sapphire and TiO$_2$ single crystal [5–7] by pulsed laser deposition. Using the HiPIMs method, VO$_2$ films are applied on glass [8], silicon with an ITO sublayer [9]. The method of magnetron reactive sputtering of a metal target in an oxygen environment allows flexible control of the phase and chemical composition of the coatings.

In this article, the results of deposition conditions influence on the chemical and phase composition of vanadium dioxide films synthesized on silicon and sapphire substrates by magnetron reactive deposition on direct current are given.

2. Research method
The experiments were carried out on the upgraded vacuum deposition unit UVN-71. The residual pressure in the chamber was less than 5·10$^{-2}$ mtorr. To create a gas environment high purity argon and oxygen are used. A magnetron with a water-cooled vanadium target (purity 99.9%) with a diameter of 115 mm operated at a constant current.
To study the composition of the discharge, the method of optical emission spectroscopy was used [10]. A typical plasma emission spectrum obtained by this method is shown in figure 1, the most informative emission lines of the emission spectrum of the discharge were chosen and their intensity was measured.

![Typical spectrum of gas discharge emission in argon atmosphere during the sputtering of a vanadium target.](image)

**Figure 1.** Typical spectrum of gas discharge emission in argon atmosphere during the sputtering of a vanadium target.

Table 1 shows the most informative emission lines, which intensity was measured. Roman numerals after the element name indicate the degree of ionization.

| Element | Line | VI (nm) | VI (nm) | OI (nm) | ArI (nm) |
|---------|------|---------|---------|---------|----------|
| Wavelength | 318.4 | 411.2 | 777.1 | 811.5 |

When removing the voltage dependence on reactive gas flow rate and the emission spectra of the gas discharge, the discharge current density was chosen as independent variables. In three experiments, the current density remained constant and was 34, 69, 104 mA/cm² (the discharge voltage was varied from 370 to 510 V). Oxygen flow rate was ranged from 0.2 to 2.6 sccm.

3. **Investigation of the gas discharge emission and influence technological process parameters on property of the films**

To determine boundaries of vanadium target operation modes during sputtering in an oxygen-containing medium is the main task of experiments. A series of experiments were carried out, some results of which are presented in figure 2. As described in the experimental conditions, fixing the current density on the target, the dependences of the intensity of argon, oxygen and vanadium lines on the reactive gas consumption were determined.

According to the results obtained using optical emission spectroscopy, it can be concluded that the behavior of a gas discharge during magnetron sputtering vanadium target in a reactive atmosphere is similar to the behavior during sputtering other metals of the transition group. The boundaries of the target operation modes (metallic, transitional and oxide) are clearly defined. Namely, the processes occurring in the gas discharge during the implementation of the metal mode are observed in the reactive gas flow rate range 0–0.2 sccm, 0–1.2 sccm, 0–2.8 sccm for a fixed current density of 34, 69, 104 mA/cm² respectively.

In the intermediate state the intensity of line VI is rapidly decreasing, while OI continues to increase. The range of values of oxygen flow rate values, which implements this mode is distinguished. Namely:

- (0.2 < Q < 0.4 sccm) for a current density of 34 mA/cm²;
- (1.2 < Q < 2.4 sccm) for a current density 69 mA/cm²;
- (2.8 < Q < 4 sccm) for a current density 104 mA/cm².
The oxide regime is characterized by the growth of the oxygen line and the exit to the saturation of the metal line. The following values of oxygen flow rate of 0.4, 2.4, 4 sccm can be called characteristic points of transition to the oxide mode for three values of current density of 34, 69, 104 mA/cm² respectively.

Changes in the voltage due to oxygen flow rate are associated with changes in the properties of the target surface, precisely the formation of an oxide film on it.

![Graph](image1)

**Figure 2.** Dependence of the intensity lines of I – VI, 2 – ArI, 3 – OI on the oxygen flow rate with argon pressure values of 0.75 mtorr for current density: a – 34, b – 69, c – 104 mA/cm².

It can be concluded that at higher current densities a greater amount of reactive gas is needed to realize the oxide mode of the target. Having determined the boundaries of the modes, it became possible to synthesize vanadium oxide films, the properties of which correlate with such technological parameters as the flow rate of reactive gas and current density. The films were deposited simultaneously on silicon and sapphire substrates at a temperature of 500 °C. As a result of X-ray powder diffraction analysis of a series of films deposited at a current density of 104 mA/cm² and oxygen flow rate of 3 sccm, the presence of the monoclinic VO₂ phase with an orientation (021) was detected.

Samples of films deposited at a current density value of 30.4 mA/cm², oxygen flow rate values of 1.8 sccm on silicon and sapphire substrates are shown in figure 3a and 3b respectively. In the sample (a) a tetragonal phase of vanadium oxide VO₂ with orientation (110) in the region of 2θ = 28 degrees are detected. In samples deposited on sapphire, there is both a tetragonal phase with a reflection plane (110) at an angle of 2θ = 28 degrees, and an orthorhombic phase of V₄O₉, which is determined at an angle of 21.6 degrees.
To characterize the phase transition, a measuring stand was used, which makes it possible to measure the dependence of the sample resistance during its heating and cooling. Using a two-probe technique, the temperature dependences of the resistance of vanadium oxide films deposited on silicon (figure 4a) and on sapphire (figure 4b) were obtained.

In samples deposited on a silicon substrate, the change in resistance was 3 orders of magnitude, while in samples obtained on a sapphire substrate, the jump in resistance was 1 order. The transition temperature in both cases was in the range of 50–70 °C. Apparently, the observed effect is due to the influence of the material and the crystal structure of the substrate on the chemical composition of the film and the orientation of crystallite growth.

4. Conclusions
The boundaries of the technological regimes are established. In these conditions vanadium oxide films VO₂ with tetragonal phase stoichiometry on silicon substrates are formed. These films are textured in the (110) direction and resistance is varied in range from 150 kΩ to 50 Ω. The study of the formation causes under the same conditions on sapphire substrates of the orthorhombic phase V₄O₉ with the preferential orientation (001) requires additional studies.

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