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Optical Properties of Vanadium Oxide Films

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As a typical Correlated Electron Material, vanadium dioxide was discovered to demonstrate metal-insulator transition at a relatively low temperature. The transition occurs from an insulating monoclinic phase to a metallic tetragonal phase (rutile structure) upon heating with the rearrangement of vanadium ions along an axis of the monoclinic lattice. The phase change corresponds to a colossal resistivity drop by over four orders of magnitude as well as other dramatic property changes, which can be reversible via a natural cooling process. Therefore, vanadium dioxide has attracted extensive attention for its applications in highly sensitive smart devices that can abruptly respond to diverse external stimuli. In recent years, rapid advancement in the fabrication and property modulation of vanadium dioxide has greatly facilitated its applications in many aspects, such as thermal sensing, thermochromics, electronics, and multiple-response mechanics. The optical properties of thin vanadium dioxide films VO_2 were researched using the modulation polarimetry technique. For VO_2 thin film deposition the two-step method was used. VO_2 films were grown on quartz glass substrates by magnetron sputtering of the VO_2 target. The films had different modifications of composition, structure, morphology, and optical properties due to the manufacturing technology. The angular dependence of the reflection coefficients of electromagnetic radiation of *s*- and *p*- polarizations and their difference for different wavelengths was measured in the paper. The polarization characteristics were simulated by a matrix transformation of the Fresnel formulas. The values of the refractive and absorption indices of the films were obtained from the condition of the best agreement between the experiment and mathematical simulation. Atomic force microscope and X-ray diffraction analysis were used as standard analytical methods.

Keywords: Modulation polarimetry technique, Polarization, VO_2 thin films, Optical properties, Reflection coefficient.

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1. INTRODUCTION

As is known, vanadium dioxide (VO_2) films are a perspective material for new electronic and photonic devices, such as thermochromic smart glasses [1-3], uncooled low-noise microbolometers [4-6], etc. These devices are commercially attractive for medical imaging [7-9], military use as night vision [10], and other technical applications [11].

Vanadium dioxide occupies a special place among metal oxides since vanadium is an element with an incomplete *d*-shell. Vanadium dioxide is characterized by the presence of strong correlation effects. VO_2 has unique properties due to the presence of electronic correlations, which are determined by the variety of types of chemical bonds between the oxygen and vanadium atoms in a given compound, including bonds due to *d*-electrons.

Crystalline vanadium dioxide is a material with a reversible fast first-order phase transition at a relatively low temperature (T = 68 °C). The transition from the monoclinic to the tetragonal phase is observed in single crystals at this temperature. The infrared (IR) sensitivity of VO_2 films is associated with huge changes in the electrical resistance and optical absorption spectra caused by the semiconductor-to-metal phase transition [12-15]. The refractive index varies from 2.5 in the monoclinic phase to 2.0 in the tetragonal phase. The jump of electrical conductivity during the phase transition for single crystals is ~ 10^5, while the material exhibits metallic conductivity with a carrier concentration of ~ 10^{22} cm $^{-3}$. Thus, VO_2 has unique properties with a variety of types of chemical bonds between oxygen and vanadium atoms.

This work aims to research the optical properties of VO_2 thin films using the modulation polarimetry technique (MP technique). The films were synthesized by the method of two-stage growth (magnetron sputtering followed by thermal annealing) [16]. Modifying the composition, structure, morphology, and optical properties of VO_2 films was achieved by changing the temperature of the substrate on which they were deposited. The angular dependences of the internal reflection of linearly polarized light R_s^2 and R_p^2, and the polarization difference ρ were measured for various wavelengths. The simulation of the indicated polarization characteristics was performed by the method of matrix transformation of the Fresnel formulas [17] for a three-layer model: glass – film – air. The refractive indices n and absorption indices k of the films were obtained from the condition of the best agreement between the experimental results and the mathematical simulation achieved by the multiparameter fitting method. We also used a combination of standard analytical methods to characterize the films: atomic force microscope and X-

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ray diffraction analysis.

To derive the practical applications of VO_2, robust control of its MIT is rather critical. It is well known that novel properties give rise to interesting applications. The adjustable MIT not only demonstrates the colossal change of electrical conductivity but it also has remarkable effects on the other properties of VO_2.

2. EXPERIMENT AND SAMPLE PREPARATION

2.1 Physical Principle of the Method

Angular polarization characteristics of VO_2 thin films were measured in Kretschmann geometry using the MP technique. The scheme of setup was described in detail in [16]. The MP technique is based on the modulation of the polarization state of electromagnetic radiation, when the orthogonal components of linearly polarized waves (perpendicular (*s*) and parallel (*p*)) polarizations are alternately transformed at a constant intensity, frequency, phase, and wave vector. The registered signal is the polarization difference $\rho(\theta) = R_s^2 - R_p^2$, which is a magnitude of difference between the intensities of the internal reflection coefficients of *s*- and *p*-polarized light (R_s^2 and R_p^2, respectively). The parameter ρ is a Q component of the Stokes vector [18]. The refractive index of the quartz half-cylinder $n = 1.45$ determines the value of the critical angle of total internal reflection as $\theta_{cr} = 43.6°$.

2.2 Sample Preparation

For VO_x thin film deposition the two-step method developed earlier was used [19-22]. VO_2 films were grown on quartz glass substrates by magnetron sputtering of the VO_2 target. The residual gas pressure was ~ $2 \cdot 10^{-6}$ Torr. During the sputtering process, the Ar/O_2 mixture pressure was kept at $3 \cdot 10^{-3}$ Torr. The power on the magnetron was ~ 10…12 W and the substrate temperature was 210 ± 5 °C. Obtained layers' thickness was 180 ± 10 nm. After deposition, the samples were annealed at 400 °C for 15 min in Ar ambient was performed. Such technological parameters of growing allow obtaining films with reduced to ~ 50 °C phase transition temperature.

For film structure modification the Ar^{2+} ion implantation was used. The energy was 180 keV and doses 0.2…5 × 10^{14} cm^{-2}. The choice of energy was made so that Ar ions create a uniform distribution of defects throughout the whole film thickness. In this paper, we present the results for samples implanted with dose 1.5 × 10^{14} cm^{-2} where the best results were obtained. At higher doses, there is a significant deterioration in the crystallinity of the film and the metal-insulator-transition parameters.

3. METHODS

The crystal structure of the films was investigated using an X'Pert Pro MPD X-ray diffractometer. The surface nanorelief of annealed vanadium dioxide films was studied using atomic force microscopy (AFM) with a scanning probe microscope NanoScope IIIa Dimension 3000TM. Measurements were performed in the tapping mode by using the ultrasharp silicon probes with a nominal tip radius of 8 nm.

4. RESULTS AND DISCUSSION

The experimental dependences of the intensities of the internal reflection coefficients of *s*- and *p*-polarized light R_s^2, R_p^2 and the polarization difference ρ on the angle of incidence of light are shown in Fig. 1 a, b. Experimental curves are shown as empty dots. Wavelengths of 632 nm (Fig. 1 a) and 750 nm (Fig. 1 b) were used for the experiment. As can be seen in the figure, the curves have a complex shape and change sign to the opposite.

Mathematically, the experimental curves can be described by the formula an equation obtained by the matrix transformation method of the Fresnel Formula for a three-layer glass-film-air model. In this model, the cluster film is considered to be flat and homogeneous with effective optical parameters [16]. The use of effective optical parameters is justified for two reasons. Firstly, the film has a slight roughness relative to the thickness according to the AFM view (Fig. 2); secondly, the film has a much smaller cluster size compared to the wavelengths used. Thus, the values of the refractive index and absorption of a thin VO_2 film can be obtained for different wavelengths from the condition that the results of mathematical simulation and experiment coincide. The coincidence was supposed to be achieved by the method of multiparameter fitting, which should not cause difficulties for a known film thickness.

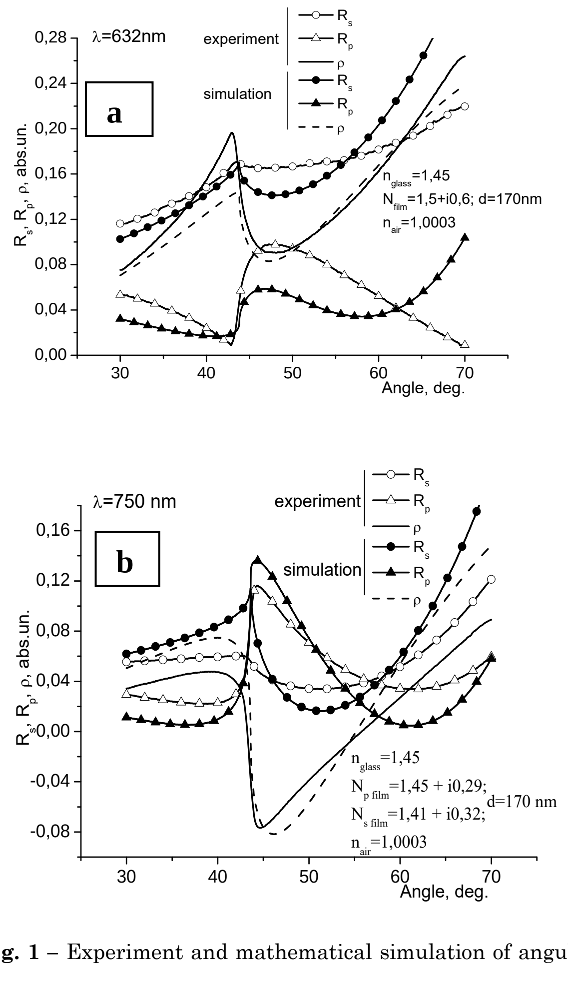

Fig. 1 – Experiment and mathematical simulation of angular

dependencies of the internal reflection coefficients R_s^2, R_p^2, and polarization difference ρ at $\lambda = 632$ nm (a) and $\lambda = 750$ nm (b)

The following optical and geometric parameters were used for mathematical simulation in Fig. 1a: refractive index of glass $n_{\text{glass}} = 1.45$ and air $n_{\text{air}} = 1.0003$; film thickness $d = 170$ nm. As a result of calculations, the value of the complex refractive index $N_{\text{film}} = 1.5 + i0.6$ for a wavelength of 630 nm was obtained. Accordingly, the refractive index of the film is $n_{\text{film}} = 1.5$, and the absorption index is $k_{\text{film}} = 0.6$.

The practice has shown that achieving an acceptable match for all three characteristics is problematic. Fig. 1a shows that the optical parameters R_s, R_p, and ρ at a wavelength of 630 nm have different correspondences. The simulation polarization difference ρ agrees best with the experimental one, while the other two dependences have a fairly large discrepancy. This discrepancy can be explained by the nonspherical shape of the clusters or their inhomogeneous distribution in the bulk of the film. The AFM study confirms this. AFM image show (Fig. 2) that the film annealing leads to the formation of the surface microcrystalline structure.

Inserting various optical parameters into the model for each of the polarized waves allows us to take this circumstance into account, as shown in Fig. 1b for a wavelength of 750 nm. For the mathematical simulation in Fig. 1b, the same optical and geometric parameters of the model for glass, air, and film thickness were used. The insertion of additional fitting parameters does not complicate the calculations, since the values of the refractive and absorption indices vary within a few hundredths. As a result of calculations, the values of the complex refractive index for *s*- and *p*-polarized waves were obtained: $N_{p\ \text{film}} = 1.45 + i0.29$, $N_{s\ \text{film}} = 1.41 + i0.32$. Accordingly, the refractive and absorption indices of the film are $n_{p\ \text{film}} = 1.45$; $k_{p\ \text{film}} = 0.29$; $n_{s\ \text{film}} = 1.41$ $k_{s\ \text{film}} = 0.32$. For unpolarized light, optical parameters can also be obtained. To do this, it is necessary to calculate the average value of these parameters. Accordingly, for a wavelength of 750 nm, the refractive index $n_{\text{film}} = 1.43$, $k_{\text{film}} = 0.305$.

The slight discrepancy between theory and experiment is explained by the film roughness, which has little effect on measurements and is not considered by mathematical simulation. The obtained values of the optical constants differ from the literature [24], their discrepancy is explained by the inhomogeneity of the film composition. Indeed, the X-ray diffraction study (Fig. 3) showed the presence of various crystalline phases in the film. The dominant crystalline phase is V_4O_9 and VO_2. A slight presence of film porosity cannot be ruled out.

Recent advances in the application of the optical properties of vanadium dioxide can be illustrated by the example of thermochromics [25]. Since VO_2 is a typical thermochromic material due to its sensitivity, there is a phase transition when the temperature changes. It demonstrates excellent regulation ability of transmittance in the IR region across MIT, while the visible transmittance remains almost unchanged. Based on this, it is a novel idea to apply VO_2-based thin film as a "smart window," which can automatically adjust the sunlight transmittance into a room (especially for the thermal effect of IR light) upon the change of ambient temperature. This device is expected to reduce huge energy consumption for indoor cooling/heating in buildings.

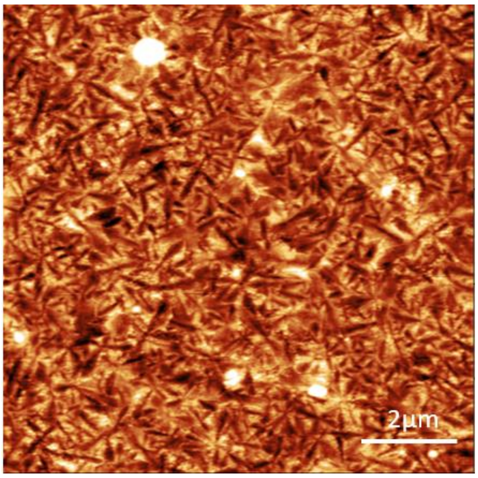

Fig. 2 – AFM top-view of the sample surface

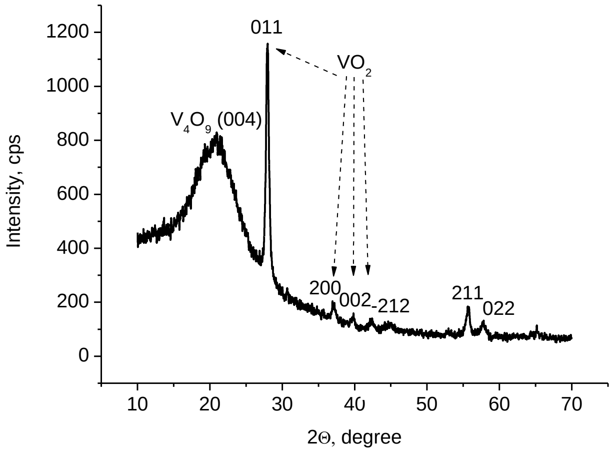

Fig. 3 – X-ray diffraction patterns of the sample

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Оптичні властивості плівок оксиду ванадію

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Як типовий корельований електронний матеріал, діоксид ванадію VO_2 демонструє перехід метал-діелектрик при відносно низькій температурі. При нагріванні відбувається перехід від діелектричної моноклінної фази до металевої тетрагональної фази (структура рутилу) з перегрупуванням іонів ванадію вздовж осі моноклінної гратки. Зміна фази відповідає колосальному падінню питомого опору більш ніж на чотири порядки, а також іншим змінам властивостей, які можуть бути оборотними через природний процес охолодження. Таким чином, VO_2 привернув велику увагу при його застосуванні у високочутливих розумних пристроях, які можуть різко реагувати на різноманітні зовнішні впливи. В останні роки швидкий прогрес у виробництві та модуляції властивостей VO_2 значно полегшив його застосування в багатьох аспектах, таких як термічне зондування, термохроміка, електроніка та механіка з множинним відгуком.

Методом модуляційної поляриметрії досліджено оптичні властивості тонких плівок діоксиду ванадію. Для осадження тонкої плівки VO_2 використовувався двоетапний метод. Плівки VO_2 вирощували на підкладках з кварцового скла шляхом магнетронного розпилення мішені VO_2 з подальшим термічним відпалом. Плівки мали різні модифікації складу, структури, морфології та оптичних властивостей, зумовлені технологією виготовлення. У роботі було виміряно кутові залежності коефіцієнтів відбивання електромагнітного випромінювання *s*- і *p*-поляризацій і їх різницю для різних довжин хвиль. Поляризаційні характеристики були змодельовані за допомогою матричного перетворення формул Френеля. Значення показників заломлення та поглинання плівок були отримані з умови найкращого узгодження між експериментом і математичним моделюванням. Як стандартні аналітичні методи використовували атомно-силовий мікроскоп і рентгенівський дифракційний аналіз.

Ключові слова: Метод модуляційної поляриметрії, Поляризація, Тонкі плівки VO_2, Оптичні властивості, Коефіцієнт відбивання.