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The optical properties of vanadium pentoxide doped with aluminum

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Abstract. This paper investigates the effect of the post-transition metal aluminum (Al) on the optical properties and band gap of thin V_2O_5 films. The transmission spectra of V_2O_5 thin films with varying Al concentrations were measured via spectrophotometry; the extinction coefficient spectra were calculated, and the optical band gap values were determined. Al doping was found to decrease the band gap of V_2O_5 films for both direct and indirect allowed interband transitions. The paper also provides an interpretation of the observed changes during alloying.

Keywords: vanadium pentoxide, thin film doping, optical band gap, band structure of V_2O_5, spectrophotometry

Introduction

Transition metal oxides represent one of the most interesting and promising classes of substances for practical applications. Due to their unfilled electronic d-shells, transition elements form complex phase systems with variable valence in compounds with oxygen, exhibiting a wide range of physicochemical properties. The introduction of a small fraction of a foreign substance into the host lattice can significantly alter its physical properties through changes in the crystal structure, the formation of new states in the band gap, or the generation of defects and/or vacancies (Bian et al 2014). Doping of transition metal oxides enables the precise regulation of their physical properties to enhance their practical utility (Abyazisani et al. 2015).

Among transition metal complexes, vanadium oxides represent a special class of materials due to vanadium's strong affinity for oxygen, resulting in various oxidation states. These oxides have strongly correlated electrons, which significantly influence their optical, magnetic, and electrical properties. Vanadium oxides find practical application in the fabrication of electronic devices, as photographic materials, optically sensitive elements, catalysts, photochromic and electrochromic materials. It is worth

noting that photochromic metal oxide materials have an advantage over other materials due to their high resistance to corrosion and heat (Volkov 1987).

Currently, many systems demonstrate photochromism, but only a few are sensitive to visible light. Visible light photochromism is potentially useful in designing compact storage devices and solar panels. In this context, vanadium oxides are of especial interest, since they are used in numerous optoelectronic devices, such as 'smart' windows (Wu et al. 2013) and thermal sensors (Chain 1991).

Vanadium pentoxide (V_2O_5) is of the greatest interest for its potential optical applications. V_2O_5 has a band gap of 2.2 to 2.7 eV, an oxidation state of +5 for vanadium, and has high chemical and thermal stability. It is used as a catalyst in chemical batteries, 'smart' windows, optical detectors, and switches. The width of the V_2O_5 band gap can be modified using dopants. To date, studies have been conducted on the effects of doping V_2O_5 with Li (Liu et al. 2015), Ti (Wei et al. 2015), Ce (Etemadi et al. 2017), W (Panagopoulou et al. 2019), and others elements. Changes in the band gap and optical characteristics were observed upon the introduction of dopant impurity atoms into the material's structure. Furthermore, it has been found that the optical properties of vanadium pentoxide thin films can be tuned through doping with transition metal and 4f-metal ions. The metal ion size and the unoccupied 3d and 4f orbitals of dopants significantly affect the band gap of the doped thin films due to the formation of impurity-induced intermediate states near the Fermi level (Kondal and Kumar 2022). However, the effect of doping vanadium pentoxide with post-transition metals remains insufficiently studied, while significant differences in the filling of electronic shells and subshells in transition and post-transition metals could lead to substantial variations in the doping effect on the optical and electronic properties of V_2O_5.

Therefore, the aim of the present study is to determine the effect of the post-transition metal Al on the optical properties and band gap of V_2O_5 thin films.

Materials and methods

The samples were synthesized in the Laboratory of Physics of Phase Transitions in Solids (Ioffe Physical-Technical Institute). Nanocrystalline films with a thickness of 80 nm were synthesized on 40 μm-thick optical mica substrates. The undoped films were synthesized by cathode sputtering of the target, followed by oxidation of metal vapors in an oxygen stream near the mica substrate. Since V_2O_5 is the highest vanadium oxide, phase verification of the obtained films was deemed unnecessary. The alloyed thin films were synthesized by the simultaneous laser evaporation of vanadium and aluminum targets in an oxygen atmosphere at a substrate temperature ranging from 750 to 900 K. The doping level within the films was controlled by varying individual evaporation time for each target.

Optical transmission spectra were measured in the wavelength range of 200–1000 nm using an SF-2000 spectrophotometer at the interdisciplinary resource center for shared use 'Modern Physicochemical Methods of Formation and Research of Materials for Industry, Science, and Education' (Herzen State Pedagogical University of Russia). Given that mica has a band gap energy significantly larger than the energies corresponding to the visible optical range under investigation, it can be confidently stated that the measured transmission spectra are characteristic of the vanadium pentoxide thin films. Visually, the samples are transparent films with a yellowish tint, which is consistent with an optical band gap of $E_g \approx 2$ eV.

Calculations were performed using computational methods based on density functional theory (DFT) with the generalized gradient approximation (GGA) (Perdew et al. 1992) and the Perdew–Burke–Ernzerhof (PBE) parameterization (Perdew et al. 1996), employing ultrasoft pseudopotentials (USPP) (Vanderbilt 1990) within the Quantum ESPRESSO package (The Quantum ESPRESSO Team… 2025). The calculations included spin-orbit coupling. The cut-off energy for the decomposition of wave functions into plane waves was 640 eV. The Brillouin zone integration was carried out using a 4 × 3 ×2 k-point grid. To account for strong electron-electron correlations, the DFT+U approach (Cococcioni 2012) was employed with a Hubbard U parameter of 5.7 eV applied to the vanadium 3d states (Jovanović et al. 2018). Dispersion interactions were included via the semi-empirical DFT-D2 correction (Grimme et al. 2011).

Results and Discussion

The transmission spectra, representing the dependence of the transmission coefficient T on the wavelength λ, were obtained using spectrophotometry. The spectrum for pure V_2O_5 is shown in Fig. 1. Since the film synthesis may result in a variation in deposition intensity across the substrate area,

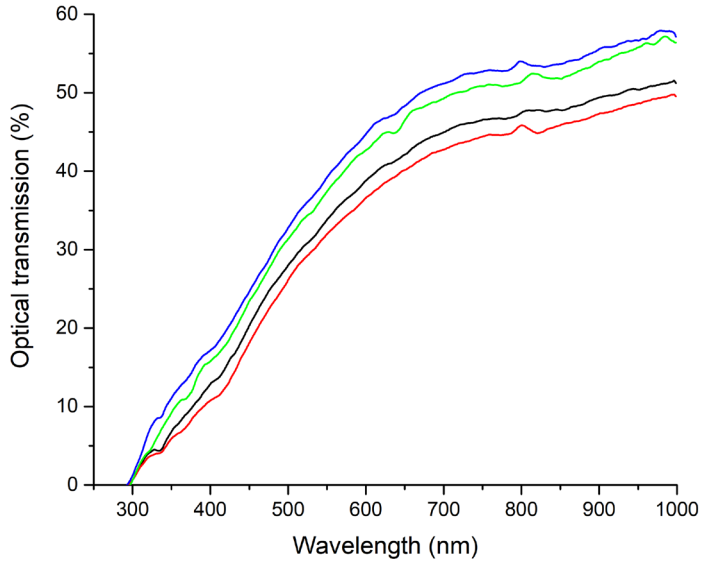

Fig. 1. Dependences of the transmission coefficient T on the wavelength λ for undoped V_2O_5 thin films

the transmittance coefficient was measured at several locations for each sample. Consequently, a series of curves were obtained and subsequently averaged for analysis.

A number of mathematical calculations are required to determine optical parameters and analyze optical characteristics (Dresselhaus 2001). The complex permittivity $\varepsilon(\omega)$ is expressed as:

$$\varepsilon(\omega) = \varepsilon' - i\varepsilon'', \tag{1}$$

where ω is the angular frequency ($\omega = 2\pi\nu$), and ε' and ε'' denote the real and imaginary parts of the complex dielectric permittivity ε, respectively.

$$\varepsilon' = n^2 - k^2,$$
$$\varepsilon'' = 2nk, \tag{2}$$

where n and k are the real and imaginary parts of the refractive index of a material.

When measuring the absorption coefficient $\alpha(\omega)$, the intensity of light ($I(d)$) after passing through a material of thickness d is compared with the intensity (I_0) of the incident light, thereby determining the absorption coefficient (α):

$$I(d) = I_0 \exp[-\alpha(\omega)d], \tag{3}$$

where

$$\alpha(\omega) = 2\frac{\omega k}{c} = 4\frac{\pi k}{\lambda}. \tag{4}$$

From this expression, it follows that the absorption coefficient $\alpha(\omega)$ is proportional to $\sim k(\omega)$, that is, the imaginary part of the complex refractive index (the extinction coefficient); therefore, k is typically associated with the loss of electromagnetic wave power.

The absorption coefficient $\alpha(\omega)$ and the photon energy were determined using formulas (5) (Schneider 2020):

$$\alpha = \frac{1}{d} ln \frac{1-R}{T},$$
$$E_{photon}[eV] = \hbar\omega = \frac{1240}{\lambda[\text{нм}]}, \tag{5}$$

where d is the film thickness, and T and R are the experimentally measured transmission and reflection coefficients of the sample.

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One of the most important parameters for evaluating semiconductor properties is the band gap (E_g), which determines the fundamental light absorption edge. The band gap of semiconductors can be determined using the following equation:

$$(\hbar\omega\alpha)^{\frac{1}{n}} = A(\hbar\omega - E_g), \tag{6}$$

where A is a constant, and n takes values of 1/2, 2, 2/3, and 1/3 for direct allowed, direct forbidden, indirect allowed, and indirect forbidden transitions, respectively. Depending on the presence of defects, dopants, or other factors, the dominant type of electronic transition may vary; therefore, this study considers both direct (7) and indirect (8) interband transitions:

$$\alpha(\omega) \sim \frac{(\hbar\omega - E_g)^{\frac{1}{2}}}{\hbar\omega}, \tag{7}$$

$$\alpha(\omega) \sim \frac{(\hbar\omega - E_g \pm \hbar\omega_{photon})^2}{\hbar\omega}. \tag{8}$$

These last two equations, known as the Tauc equations, are used to determine the band gap (E_g) of semiconductors. Fig. 2 shows the mechanisms of direct and indirect interband electronic transitions in semiconductors (Schneider 2020).

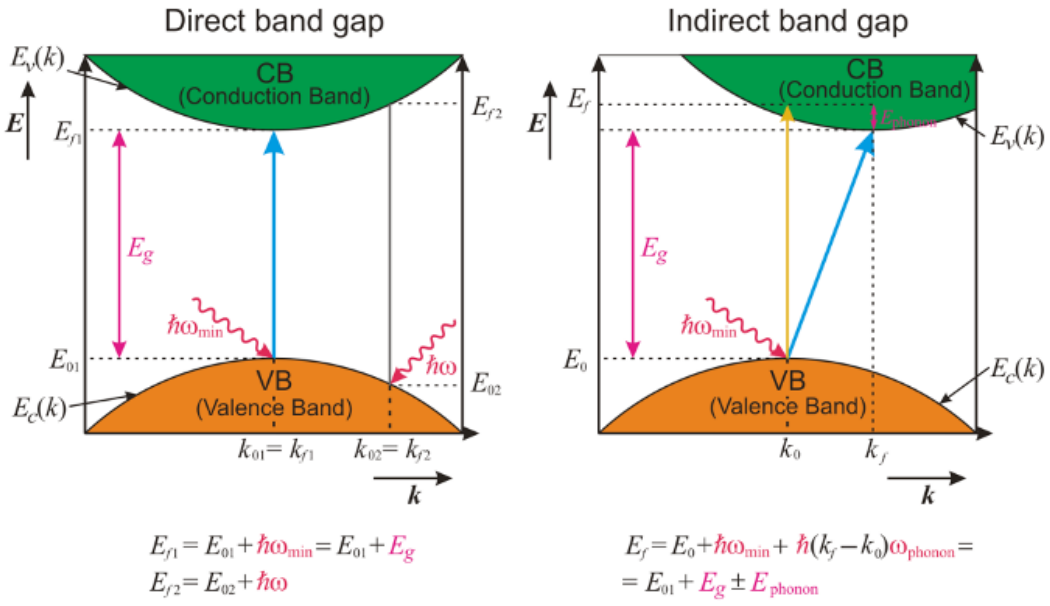

Fig. 2. Mechanisms of interband electronic transitions (Schneider 2020)

With a known transmission coefficient T, the absorption coefficient α can be obtained using formula (9):

$$\alpha = -\frac{\ln T}{d}. \tag{9}$$

Using the coefficient α, the optical spectrum of the extinction coefficient k as a function of the wavelength λ is calculated (Fig. 3). For this, we obtain from formula (4):

$$k = \frac{\alpha\lambda}{4\pi}. \tag{10}$$

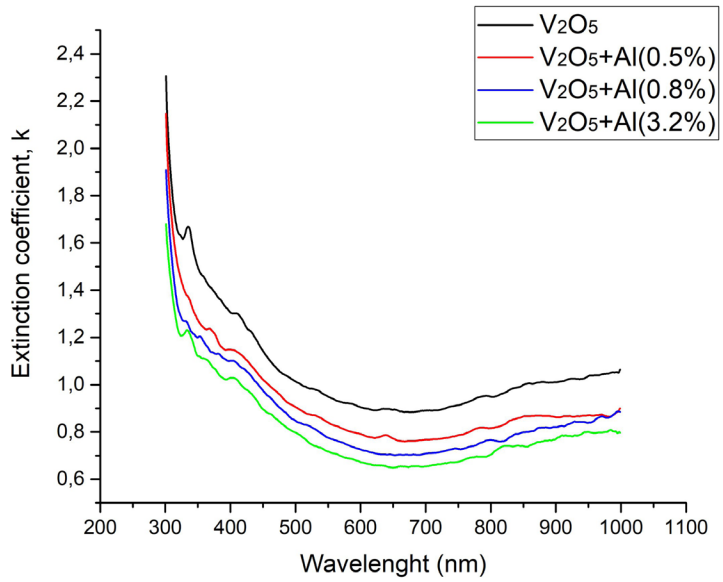

Fig. 3. Dependence of the extinction coefficient on the wavelength for V_2O_5, V_2O_5+Al (0.5%), V_2O_5+Al (0.8%) and V_2O_5+Al (3.2%)

The graph shows that dependencies for all the obtained curves are very similar. However, the extinction coefficient k decreases with an increasing percentage of aluminum. Thus, it has been found that the dopant Al influences the optical characteristics of the film by enhancing its transmission capacity.

Knowing the wavelengths, we can proceed to the values for the frequency ω using formula (11):

$$c = \lambda\omega, \tag{11}$$

where c is the speed of light ($c = 3 \cdot 10^8$ m/s).

From formulas (7) and (8) we obtain:

$$(\alpha\hbar\omega)^2 = \hbar\omega - E_g,$$

$$(\alpha\hbar\omega)^{\frac{1}{2}} = \hbar\omega - E_g \pm \hbar\omega_{photon}, \tag{12}$$

where the photon energy $\hbar\omega_{photon}$ is usually neglected, since it is several times less than the electronic transition energy.

The dependencies shown in Figures 4 and 5 were constructed using formulas (12). Using the extrapolation method, the optical band gap parameters for undoped and doped vanadium pentoxide samples were determined.

To determine the dominant type of optical transition in vanadium pentoxide, calculations were performed within the framework of density functional theory (Fig. 6.). The calculation result of E_g =2.43 eV, when compared with the experimentally obtained values, indicates that indirect electronic transitions dominate in the material.

From the graphs, it can be observed that as the impurity concentration increases, the optical band gap decreases from a value of E_g = 2.45 eV in pure vanadium pentoxide to E_g = 2.33 eV in the sample doped with 3.2% Al.

When V_2O_5 is doped with Al atoms, two factors influence the optical characteristics of the materials. The first factor is the difference in the ionic radii of vanadium and aluminum atoms. The ionic radius of the V^{5+} ion is approximately 68 pm, and that of Al^{3+} is 57 pm. Thus, the substitution of vanadium atoms by aluminum atoms induces compressive strain in the structure, leading to significant internal stresses in the crystal lattice and an increase in the average material density. However, this primarily affects the refractive index n.

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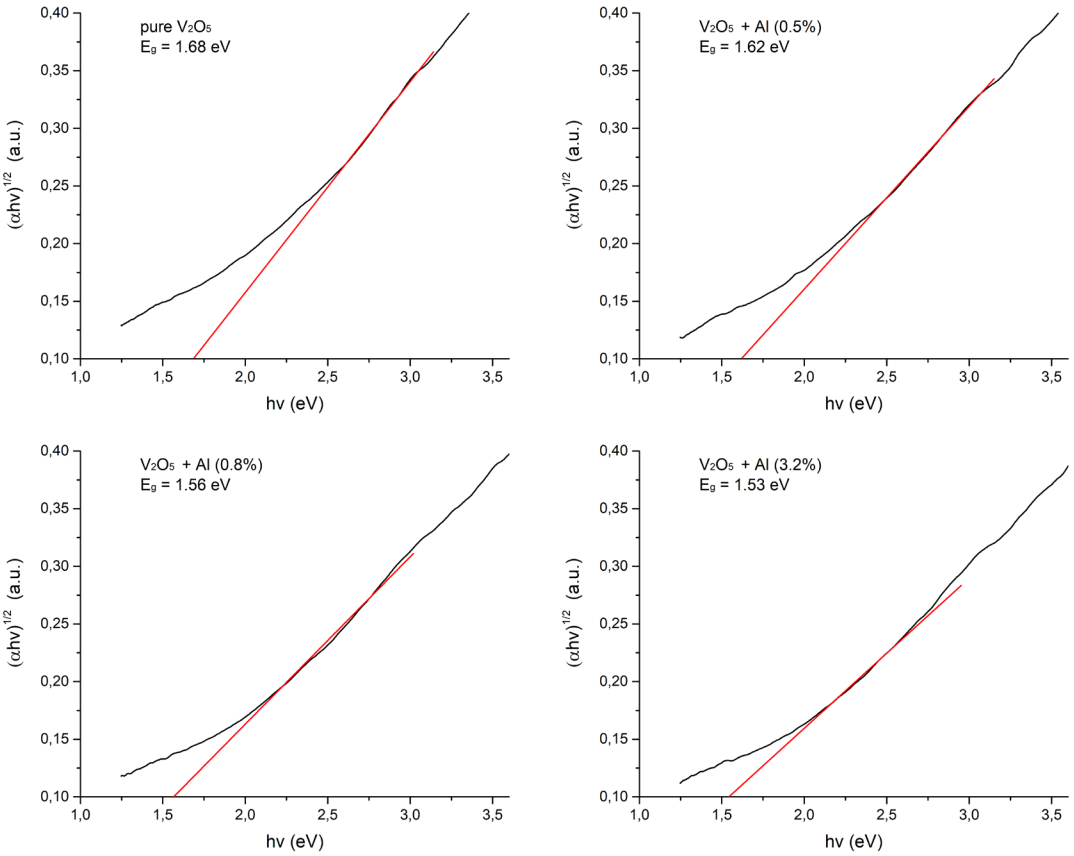

Fig. 4. Determination of the optical band gap for direct transitions in V_2O_5, V_2O_5+Al (0.5%), V_2O_5+Al (0.8%) and V_2O_5+Al (3.2%)

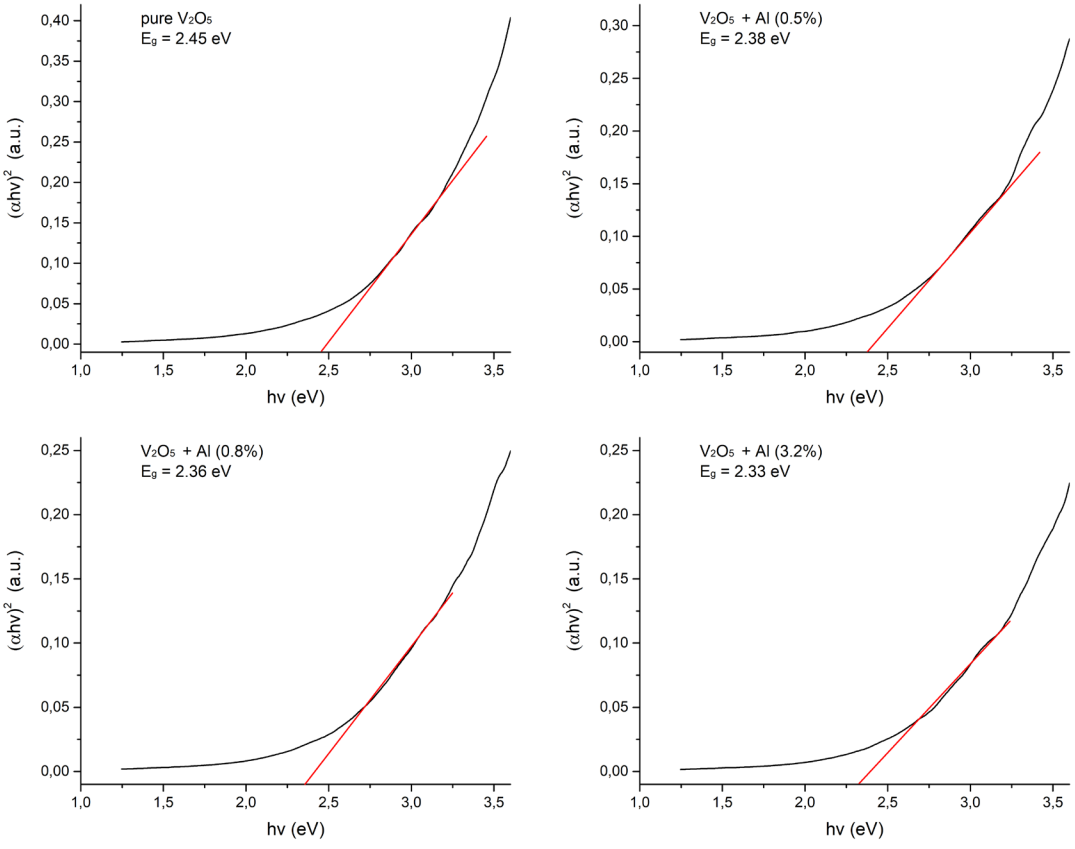

Fig. 5. Determination of the optical band gap for indirect transitions in V_2O_5, V_2O_5+Al (0.5%), V_2O_5+Al (0.8%) and V_2O_5+Al (3.2%)

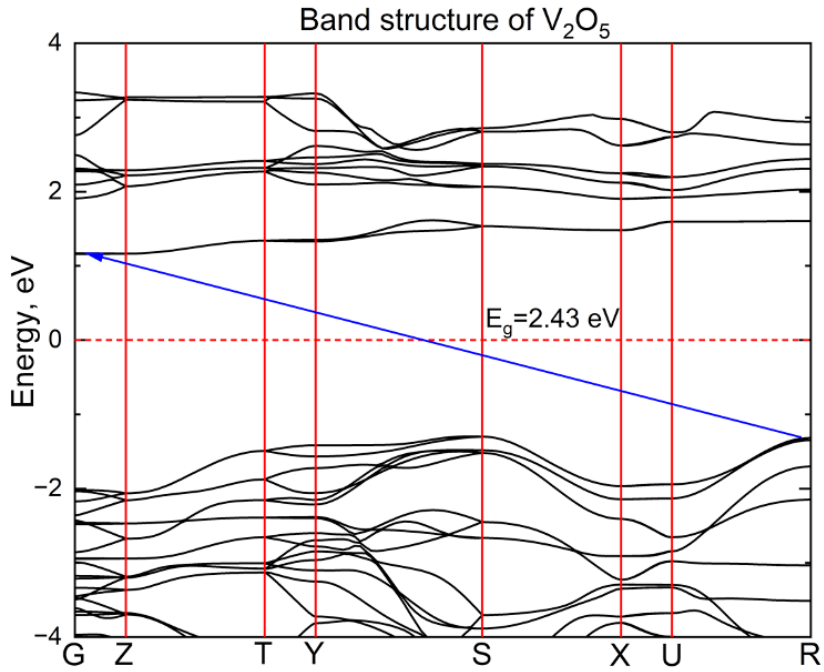

Fig. 6. Band structure of V_2O_5

The extinction coefficient *k* is influenced by the band gap width, the type of transition, and the presence of impurity energy levels. In the case of doping vanadium pentoxide with aluminum, V with a valence of 5 is replaced by Al with a valence of 3. This substitution effectively increases the hole concentration in V_2O_5. In this context, Al atoms act as an acceptor impurity, creating acceptor levels within the band gap, which facilitates interband transitions and reduces the band gap of the material.

Conclusion

This work investigated the optical properties of thin vanadium pentoxide films doped with Al. It was found that with increasing aluminum concentration, the extinction coefficient *k* decreases in the visible wavelength range, and the optical band gap decreases from E_g = 2.45 eV in undoped vanadium pentoxide to E_g = 2.33 eV in a sample doped with 3.2% Al for the case of an indirect allowed interband transition. The observed effect is attributed to an increase in the hole concentration in V_2O_5 when vanadium with a valence of 5 is replaced by aluminum with a valence of 3, which narrows the band gap due to the formation of acceptor levels.

Conflict of Interest

The authors declare that there is no conflict of interest, either existing or potential.

Author Contributions

Aleksei A. Kononov wrote the manuscript; Pavel S. Provotorov performed experimental studies, processed and analyzed the results; Leonid Yu. Orlov performed first-principles calculations to compare the band structure of the material with the experimental results; Vladimir A. Klimov synthesized the samples. All authors took part in the discussion of the final version of the article.

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