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Investigation of optical and physico-chemical properties of titanium-doped V_2O_5 nanofilms

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ABSTRACT
In this paper, undoped and Ti-doped V_2O_5 thin films were fabricated and deposited onto glass substrates using a «doctor blading» method. Then, the effects of Ti-doping on the optical properties of the thin films were investigated. Titanium doping concentration of 0.25-0.75 at.% has been investigated. After treatment in air at different temperatures, the obtained films was characterised by various techniques such as scanning electron microscopy (SEM), X-ray diffraction (XRD) and photoluminescence (PL). It was found that the as-obtained doped films possessed thermochromic properties and optical switching characters. According to optical tests, thin linings of vanadium dioxide alloyed with Ti have optical properties that are effective for application. Because of their capacity to automatically control interior solar irradiation, lower air-conditioning energy consumption, and maintain a comfortable internal thermal climate, smart windows have drawn increased interest in recent years. The doping strategy and integrating with functional coatings can regulate the properties of obtained V_2O_5 films.
Keywords: vanadium pentoxide, nanofilms, doping, smart windows, optical properties.

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Introduction

Vanadium dioxide is a material that experiences a metal–conductor phase transition at a temperature of 67 °C. This phase transition is a transition of the first kind with a latent transition heat of 4190 kJ/mol or 1000 kcal/mol. During such a transition, both the optical and electrical constants of the material experience a change. Above a temperature of 67 °C, the material has metallic conductivity, at a temperature below 67 °C, the material has semiconductor properties [[1], [2], [3]]. The conductivity of the material of sunlight, infrared rays decreases 3-5 times. In connection with the above-mentioned properties, scientific and technical interest in the optical and thermo-optical properties of vanadium oxides films used in the production of smart windows is growing [[4], [5]]. After applying vanadium gels to the substrate (by pulverization or centrifugation) and carrying out some additional technological operations, it is possible to obtain thin films of appropriate compositions on the surface of the substrate. Among the modern methods of thin film synthesis (magnetron sputtering and electron beam evaporation, laser ablation, decomposition and gas-phase chemical deposition of organometallic compounds, anodic, including plasma, oxidation, etc.), a special place is occupied by liquid-phase deposition (LPD) methods [[6], [7], [8]]. The advantages of LPD methods for producing thin films are as follows. Liquid phase deposition allows films to be applied directly to substrates in such simple ways as immersion, pulverization or centrifugation. Unlike vacuum methods, in this case, the use of complex expensive equipment is not required. In addition, the films can be applied to large surfaces and substrates of complex shape [[9], [10]]. The main reason for this increase in interest is the specifics of the optical properties of vanadium coating, which is often alloyed with variable valence metals. That is, these alloy coatings, which are made on the surfaces of glass windows, have the property of "regulating" the sun's rays when used to construct buildings. The mechanism of the "regulatory" property of such sunlight can be explained by the following phenomenon [[11], [12], [13]]. During alloying with some metals, vanadium oxide is partially filled with d-orbitals and form a complex chemical structure. Under the influence of this, the nanoparticle coating applied to the surface of a glass window forms the properties of metal bonds and the variability of optical conductors. Under the influence of a small increase in the temperature that occurs in the packaging materials when the sun goes down, the electrons move from the lower d-Orbital to the higher-energy free orbital, resulting in the formation of conductive electrons and space in the packaging structure [[14], [15]].

There is another theory describing this phenomenon, which is interpreted as follows. When an electron moves in narrow zones, its kinetic energy is comparable to the energies of electron-phonon and interelectronic interactions, which can lead to the disappearance of the initial metallic state with the appearance of a dielectric gap in the electronic spectrum. Thus, it is the specific features of d and f unfilled electron shells that are the cause of the unique properties of transition and rare earth metal compounds, and f-electrons are relatively highly localized, and the behavior of d-electrons combines both band and atomic (localized) properties at the same time [[16], [17], [18]].

The resulting materials - Smart windows - are gaining popularity due to a wide range of advantages, such as multifunctionality, matte covering, light scattering at different angles. Thanks to the use of unique glazing, heat loss and energy costs are significantly reduced, glass can be used simultaneously as curtains or blinds, creating shade or letting light in sunny and clear weather [19]. By using of Smart glass for decorative purposes, the color range and practicality, ease and speed of modernization with adhesives increase. In general, the global smart glass market is currently developing very rapidly and in the next few years the Smart glass market will only grow, discovering new features and introducing unique technologies [20].

In the present work, vanadium oxide co-sputtered with titanium on quartz substrates. Resulted coatings are the characterstic by X-ray diffraction (XRD) and scanning electron microscopy (SEM) techniques. The optical properties of the film are evaluated by photoluminescence (PL).

Experimental Details

To apply thin films of vanadium and titanium alloy (V-Ti) to the surface of the matrix layer, the "doctor blading" method was chosen. Alloying of vanadium oxide with titanium was carried out from 0.25 % to 0.75 %. The geometric parameters of the applied films were controlled by the number of cycles. Each cycle consists of applying a well-mixed suspension of V-Ti nanoparticles, polyethylene glycol and distilled water. The alloy (V-Ti) is prepared using nanoparticle powders, 25 nm in size. The proportion of V-Ti to polyethylene glycol is 0.96 g. per 2 ml, respectively. For magnetron sputtering of thin films, the MAGNA TM-200-1 magnetron sputtering unit was used. The formation of thin films on the glass surface by magnetron deposition proceeded in the mode of operation of the energy source at direct current. The deposition process was accompanied by feeding into a chamber with a high vacuum ($2.95 \cdot 10^{-5}$ millibars) mixtures of working gases argon (99.95%) and oxygen (99.92%). The elimination of oxides from the surface of the metal target was achieved by pre-spraying the vanadium target material in argon plasma for 15-25 minutes. The physical atomization of the V-Ti alloy proceeded by bombarding the surface of a vanadium target with accelerated ions of sputtering argon gas, the purity of which was 99.98%, followed by the reaction of vanadium atoms torn from the target surface with reactive oxygen gas. The supply of argon and oxygen gases was carried out through channels of independent gas intakes with controllers of a mass gas flow meter. The magnetron's power was 500 watts. The subsequent treatment consists in drying in an atmosphere of air (bringing to the state of a gel layer) and heat treatment. Heat treatment consists of two stages: calcination and annealing. Annealing of the formed coating at a temperature of 130 °C for 15 minutes reduces the level of cracking of the film. Annealing of the coating makes it possible to remove residual and by-product polymer molecules from the surface, and also improves crystallinity. The annealing temperature is 500 °C, the duration is 2 hours. X-ray studies were carried out using a Panalytical Epsilon 4. Energy-dispersive spectroscopy (EDS) analysis was performed on the basis of a MIRA 3 TESCAN scanning probe microscope with energy dispersive prefixes for microprobe analysis.

Results And Discussion

The XRD structural analysis spectrum shown in Figure 1 demonstrates the main peaks related to the anatase phase, with small inclusions of the rutile phase. Also, the XRD structural analysis revealed the orientation of orthorhombic V_2O_5 crystallites according to the file (JCPDS:00-041-1426) in the growth directions (101), (301), (011) and (020) corresponding to 2 theta 26.1°, 32.4°, 34.3°.

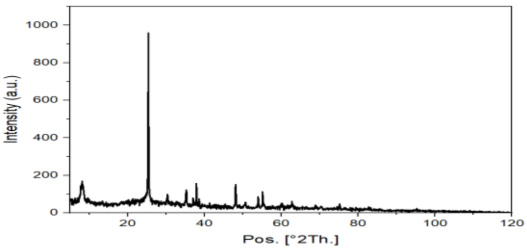

Figure 1- XRD patterns of V_2O_5/TiO_2 films

The morphology of the sample obtained by hydrothermal synthesis of TiO_2 was studied by Tessap scanning electron microscopy (Figure 2). A uniform array of TiO_2 structures consists of rods with a diameter of 170-200 nm, directed mainly perpendicular to the substrate. The remaining peaks belong according to the card file (JCPDS: 01-078-1510) to the faces of anatase/rutile TiO_2 crystals (110), (101), and (211).

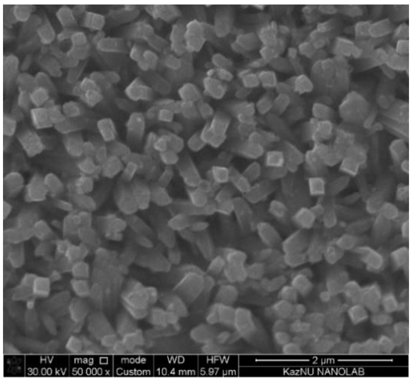

Figure 2 - SEM image of the morphology of the TiO_2/V_xO_y coating surface.

The study of the morphology of the obtained samples shows the formation of uniform V_2O_5/TiO_2 coatings with rare inclusions of objects with large dimensions (relative to the surface) related to coatings (Figure 3 (a-b)). In Figure 3 (c-d), the film growth boundary is clearly visible, created to understand the nature of the coating.

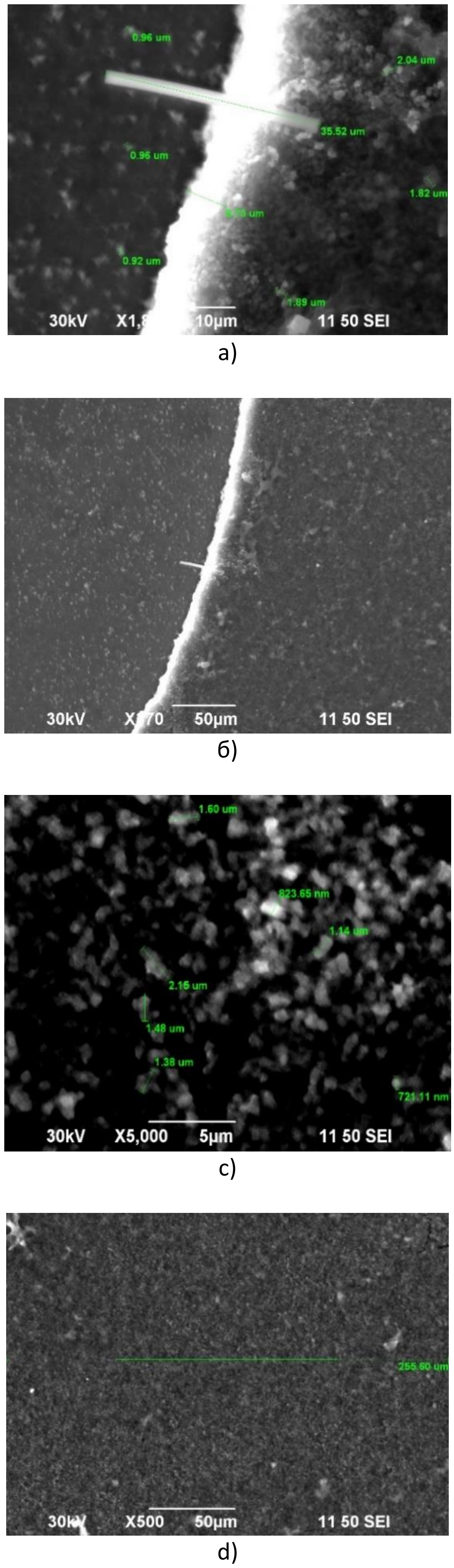

Figure 3 - SEM images of the surface morphology of V_2O_5/TiO_2 nanocomposites

The figure shows that the section appears with a sharp protrusion on the surface of the sample. After applying layers of TiO_2 nanoparticles to create a V_2O_5/TiO_2 nanocomposite, the surface consisted of microspheres, the average size of which varies from 0.9 to 2 microns (Figure 3 (a, b)).

When applying TiO_2 thin films in the amount of 5 "doctor blading" cycles, the average particle size evenly distributed on the sample surface does not increase (Figure 3 (c, d)).

The study of the morphology of the obtained samples shows the formation of uniform V_2O_5/TiO_2 coatings with rare inclusions of objects with large dimensions (relative to the surface) related to coatings (Figure 3 (a-b)). In Figure 3 (c-d), the film growth boundary is clearly visible, created to understand the nature of the coating.

Table 1 - Optical properties of the obtained coatings.

№	Components of the coating	W Doping level, %	IR reflectance / %	Solar reflectance / %
1	V_2O_5	-	27	18
2	V_2O_5 +Ti	0.25	31	29
3	V_2O_5 + Ti	0.50	33	34
4	V_2O_5 + Ti	0.75	34	39

Table 1 shows some optical properties (IR and Solar reflectance) of the samples in order to determine the possible of practical application of the obtained coatings. As Table 1 indicates, the coating that consists of only vanadium pentoxide reflects only 18.0 % of the sun's rays; when doped with 0.75 % titanium, the percentage of reflection increased to 39.0 %. The properties of reflectance of infrared rays were also studied. According to the research results, when alloying titanium pentoxide with 0.25 % to 0.75 %, the degree of reflection of infrared rays increased from 27.0 % to 34.0 %.

Conclusion

Titanium–vanadium oxide films with various compositional ratios were prepared by magnetron sputtering deposition and then the optical and physico-chemical properties were examined. The XRD analysis shows the amorphous nature of Ti-doped nanofilms. SEM images reveal columnar nanorod, that confirms the nano structure of the fabricated film. Furthermore, the optical switching property of obtained TiO_2/V_xO_y was studied and it was found that it possessed good thermochromic properties and optical switching characters.

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Титанмен легирленген V_2O_5 наноқаптамасының оптикалық және физика-химиялық қасиеттерін зерттеу

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ТҮЙІНДЕМЕ

Бұл жұмыста легірленбеген V_2O_5 және V_2O_5 - тің титанмен легірленген қоспалары жасалып «доктор блейдинг» әдісімен шыны субстраттар бетін қаптауға қолданды. Алынған қаптамалардың физико-химиялық және оптикалық қасиеттері зерттелді. Ванадий пентаоксидін легірлеуде титан концентрациясы 0,25-0,75 %-ды құрады. Алынған қаптамаларды сканерлейтін электронды микроскопия (SEM), рентгендік дифракция (XRD) және фотолюминесценция (PL) сияқты әртүрлі әдістермен зерттелді. Легірленген қаптамалар термохромды және оптикалық қасиеттерге ие екендігі анықталды. Оптикалық сынақтарға сәйкес, Ti-мен легирленген ванадий диоксидінің жұқа қаптамалары тұрмыста қолдануға тиімді оптикалық қасиеттерге ие екендігі анықталды. Өзінің тұрғын үйлер мен кеңселер ішіндегі күн сәулесін автоматты түрде реттеу, қолданылатын кондиционерлердің энергия тұтынуын төмендету және ішкі жылу жағдайларын тиімді деңгейде ұстау қабілетінің арқасында "смарт терезелерге" соңғы жылдары қызығушылықты арттыруда. Легирлеу дәрежесі және функционалды жабындармен біріктіру, алынатын V_2O_5 пленкаларының әртүрлі қасиеттерін алуға мүмкіншілік беретіні анықталды.

Түйін сөздер: ванадий пентоксиді, наноқаптамалар, легірлеу, смарт терезелер, оптикалық қасиеттер

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Исследование оптических и физико-химических свойств нанопокрытия V_2O_5 легированного титаном

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АННОТАЦИЯ

В работе были изготовлены тонкие нанопокрытия, состоящие из нелегированного V_2O_5 и легированного с титаном V_2O_5 которые были нанесены на стеклянные подложки методом «doctor blading». Изучены физико-химические и оптические свойства полученных покрытии. При легировании пентаоксида ванадия концентрация титана составляла 0,25-0,75%. Полученные покрытия были исследованы различными методами, такими как сканирующая электронная микроскопия (SEM), рентгеновская дифракция (XRD) и фотолюминесценция (PL). Установлено, что легированные покрытия обладают термохромными и оптическими свойствами. Согласно оптическим испытаниям, было установлено, что тонкие пленки оксида ванадия, легированные с Ti, обладают оптическими свойствами, эффективными для использования в быту. Благодаря своей способности автоматически регулировать солнечное излучение внутри помещений, снижать энергопотребление кондиционеров и поддерживать комфортный внутренний тепловой климат, "умные окна" в последние годы вызывают повышенный интерес. Определено, что стратегия легирования и интеграция с функциональными покрытиями могут регулировать свойства получаемых пленок V_2O_5.

Ключевые слова: пентоксид ванадия, нанопокрытия, легирование, смарт-окна, оптические свойства

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References

[1] Ciampi G, Rosato A, Scorpio M, Sibilio S. Retrofitting solutions for energy saving in a historical building lighting system. Energy Procedia. 2015;78:2669-2674, https://doi.org/10.1016/j.egypro.2015.11.343

[2] Zhilkashinova A, Abilev M, Pavlov A, Prokhorenkova N, Skokov M, Gradoboev A, Zhilkashinova A. Ion-Plasma Spraying and Electron-Beam Treatment of Composite Cr-Al-Co-ZrO_2-Y_2O_3 Coating on the Surface of Ni-Cr Alloy. Coatings. 2021;11:321-325, https://doi.org/10.3390/coatings11030321

[3] Piccolo A, Simone F. Performance requirements for electrochromic smart window. Journal of Building Engineering. 2015;3:94-103, https://doi.org/10.1016/j.jobe.2015.07.002

[4] Aimaganbetov KP. Review of experimental and theoretical research works of smart windows. Kompleksnoe Ispolzovanie Mineralnogo Syra = Complex Use of Mineral Resources. 2019;3(310):34-40, https://doi.org/10.31643/2019/6445.26

[5] Fernandes LL, Lee ES, Ward G. Lighting energy savings potential of split-pane electrochromic windows controlled for daylighting with visual comfort. Energy and Buildings. 2013;61:8-20, https://doi.org/10.1016/j.enbuild.2012.10.057

[6] Zhilkashinova A, Abilev M, Zhilkashinova A. Microplasma-Sprayed V_2O_5/C Double-Layer Coating for the Parts of Mini-Hydropower Systems. Coatings. 2020;10:725-736, https://doi.org/10.3390/coatings10080725

[7] Soltani M. Thermochromic vanadium dioxide smart coatings grown on Kapton substrates by reactive pulsed laser deposition. Journal of Vacuum Science and Technology A. 2006;24(3):612-621, https://doi.org/10.1116/1.2186661

[8] Ilahi B, Abdel-Rahman M, Zaaboub Z, Zia MF, Alduraibi M, Maaref H. Thermal annealing induced multiple phase in V/V_2O_5 alternating multilayer structure. International Journal of Modern Physics B. 2016;30:1650210, https://doi.org/10.1142/S0217979216502106

[9] Zia MF, Abdel-Rahman M, Alduraibi M, Ilahi B, Alasaad A. Synthesis and electrical characterization of vanadium oxide thin film thermometer for microbolometer applications. Electronics Letters. 2016;52:827-828, https://doi.org/10.1049/el.2016.0017

[10] Zia M, Abdel-Rahman M, Alduraibi M, Ilahi B, Awad E, Majzoub S. Electrical and infrared optical properties of vanadium oxide semiconducting thin film thermometers. Journal of Electronic Materials. 2017;46:5978-5885, https://doi.org/10.1007/s11664-017-5571-0

[11] Abdel-Rahman M, Alduraibi M, Zia M, Bahidra E, Alasaad A. Vanadium sesquioxide (V_2O_3)-based semiconducting temperature sensitive resistors for uncooled microbolometers. Modern Physics Letters B. 2017;31:1750145, https://doi.org/10.1142/S0217984917501457

[12] Chen X, Dai J. Optical switch with low-phase transition temperature based on thin nanocrystalline VOx film. Optik. 2010;121: 1529-1533, https://doi.org/10.1016/j.ijleo.2009.02.016

[13] Zhou X, Meng Y, Vu TD, Gu D, Jiang Y, Mu Q, Li Y, Yao B, Dong Z, Liu Q, Long Y. A new strategy of nanocompositing vanadium dioxide with excellent durability. Journal of Materials Chemistry A. 2021;9:15618-15628, https://doi.org/10.1039/d1ta02525b

[14] Chang T, Cao X, Li N, Long S, Zhu Y, Huang J, Luo H, Jin P. Mitigating deterioration of vanadium dioxide thermochromic films by interfacial encapsulation. Matter. 2019;1:734-744, https://doi.org/10.1016/j.matt.2019.04.004

[15] Zheng J, Bao S, Jin P. TiO_2 (R)/VO_2 (M)/TiO_2 (A) multilayer film as smart window: combination of energy-saving, antifogging and self-cleaning functions. Nano Energy. 2015;11:136-145, https://doi.org/10.1016/j.nanoen.2014.09.023

[16] Moein M, Binions R. Sol-gel approaches to thermochromic vanadium dioxide coating for smart glazing application. Solar Energy Materials and Solar Cells. 2017;159:52-65, https://doi.org/10.1016/j.solmat.2016.08.035

[17] Chang T, Cao X, Dedon LR, Long S, Huang A, Shao Z. Optical design and stability study for ultrahigh-performance and long-lived vanadium dioxidebased thermochromic coatings. Nano Energy. 2018;44:256-264, https://doi.org/10.1016/j.nanoen.2017.11.061

[18] Rezaei SD, Shannigrahi S, Ramakrishna S. A review of conventional, advanced, and smart glazing technologies and materials for improving indoor environment. Solar Energy Materials and Solar Cells. 2017;159:26-51, https://doi.org/10.1016/j.solmat.2016.08.026

[19] Liu Y, Tao H, Chu X, Wan M, Bao J, Zhao X. Effects of addition of tungsten chloride on optical properties of VO_2-based thermochromic films prepared by sol-gel method. Journal of Non-Crystalline Solids. 2014;383:116-120, https://doi.org/ 10.1016/j.jnoncrysol.2013.04.043

[20] Bae SH, Lee S, Koo H, Lin L, Jo BH, Park C, Wang ZL. The memristive properties of a single VO_2 nanowire with switching controlled by self-heating. Advanced Materials. 2013;25:5098-5103, https://doi.org/10.1002/adma.201302511