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SYNTHESIS OF VANADIUM DIOXIDE THIN FILMS AND NANOPOWDERS: A BRIEF REVIEW

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Abstract. Vanadium dioxide (VO_2) undergoes semiconductor-metal phase transition (SMPT) at the ambient temperature. Due to this fact, it becomes perspective material for thermo sensors, thermo switchers, optical switchers and shutters, IR sensors, thermochromic coatings, smart coatings for glasses, holographic elements, and elements of energy-independent memory. By now, there is no doubt that the characteristics of SMPT depend on VO_2 morphology. Morphology, in turn, depends on the synthetic procedure. In this review, we survey the methods of synthesis of VO_2 thin (micro- and nanosized) films and nanopowders; namely, chemical vapour deposition (CVD), physical vapour deposition (PVD), sol-gel method, atomic layer deposition (ALD), and hydrothermal synthesis. The peculiarities of the morphology of synthesized products will be discussed regarding for the conditions of synthetics procedures.

1. INTRODUCTION

Among inorganic materials with semiconductor-to-metal phase transition, the great importance has vanadium dioxide [1]. Scientific interest is caused by the fact that the nature of this transition remains still not clear [2,3]. The discussion about the factor that initiates this phase transition is nowadays continued in many publications that describe synthesis and applications of vanadium dioxide. On the other hand, the known experimental data about the change of electrical and optical properties at semiconductor to metal phase transition indicate wide perspective for practical use of this oxide. Vanadium dioxide is successfully used in termosensitive elements as well as in the devices for holograms registration. It is also proposed as the material for smart windows. Moreover, the new promising areas of VO_2 application are now intensively studied. The characteristics of phase transition are influenced by wide range of additional factors, e.g. morphology, dimensionality of the structure, stoichiometry, doping, and crystallography of low temperature phase. This provides the wide possibilities for investigation both from practical and fundamental points of view.

In this review, the methods and technology of the synthesis of two- and three-dimensional VO_2-based structures are discussed.

2. SYNTHESIS OF VO_2 THIN FILMS

Vanadium dioxide thin films are usually synthesized by means of chemical vapour deposition (CVD), physical vapour deposition (PVD), and sol-gel method. A number of studies on the synthesis by atomic layer deposition method are also known. As supports, titanium dioxide, tin dioxide or silica, as well as platinum, silicon, sapphire etc. can be used depending on the synthetic procedures. All the authors have noted a direct dependence between the synthesis methods and conditions and products physical and chemical properties, and stoichiometry. Moreover, the film morphology also greatly influences

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the phase transition characteristics, especially on the electrical hysteresis loop width. Besides VO_2, there are homologous vanadium oxides that are also known as Magnelli phases V_nO_{2n-1} [4]. If the synthesis method is based on the reduction of vanadium higher oxidation states and the oxidation of lower ones, the careful choice of synthetic conditions is required in order to provide pure VO_2 instead of some other vanadium oxides. This fact is of great importance while synthesizing vanadium dioxide thin films.

CVD is well-known commercial method for obtaining high purity solid inorganic coatings. The survey of CVD application for VO_2 synthesis is given in [5]. The description of modern experimental process and the study of films growth mechanism are presented in [6]. The variation of synthetic conditions causes the changing of the product morphology. For example, varying the deposition temperature (500 or 150 °C) within CVD procedure, it is possible to produce V_2O_5 rods or VO_2 microblocks on the glass surface using vanadium(IV) acetylacetonate as the precursor [7]. Besides, this method allows synthesizing W-doped [8] and F-doped [9] thin films on the glass surface.

PVD experiment can be organized in different modes; sputtering and deposition are mainly used for VO_2 thin films synthesis. In the case of sputtering, initial target bombardment by ionic stream is used. The formed gas subsequently condensed on the substrate. In the deposition case, the material evaporates and then precipitates on the substrate in the Ar/O_2 atmosphere or in plasma.

Ion-beam sputtering of metallic vanadium on silicon surface requires subsequent oxidation of the film [10]. The key factors here are: oxygen pressure in the work chamber, temperature, reaction time, and degree of the initial substrate purity. In the case of laser ablation, the synthesis is carried out using 99.9% metallic vanadium target [11] under strict control of the substrates temperature and oxygen pressure in the work chamber. The above-mentioned factors are of the highest importance. Each substrate requires the careful choice of synthesis conditions in order to obtain VO_2 formation instead of other vanadium oxides, see, e.g., [12] and [13], where Magnelli phases were obtained on TiO_2 (110) and SnO_2 (110), respectively. The mixture of different vanadium oxides is also formed on anatase (001), the specific composition depends on the temperature of oxygen plasma-assisted molecular beam epitaxy process as well as on the number of layers [14]. Recently, a wide range supports for VO_2 thin films synthesis is suggested. For example, RF magnetron sputtering technique was used in [15] to synthesize VO_2 films on indium tin oxide (ITO)-coated glass substrates. In this case, the presence of an ITO sublayer also seems to result in smaller grain size and slightly broader hysteresis in VO_2 films. Model conducting oxide underlayers (Nb-doped $SrTiO_3$ and RuO_2 buffered TiO_2 single crystals) were used as a support in [16]. VO_2 film can be also obtained from V_2O_5 film on silicon substrate by reduction method. For example, RF-sputtered films of V_2O_5 on Si(001) can be converted into either VO_2(B) or VO_2(M/R) (with100 to 120 nm thickness) depending on the reduction conditions [17].

Considering the results of [18,19], it can be concluded that the oriented growth of VO_2 films on the surfaces of different supports can be obtained using sputtering method. The pevident dependence between phase transition temperature and substrate temperature in magnetron sputtering method should be also noted [20].

Pulsed laser deposition (PLD) is an alternative approach widely used for VO_2 thin films synthesis. Authors of [21] report of VO_2 and TiO_2 heteroepitaxial bilayers deposition on alumina surface; it is stated that the phase transition temperature depends on the support orientation; in this case, the above temperature varies in a wide range. This fact was explained by the change of oxygen content in vanadium dioxide and/or by the support deformation. However, it can be also the result of Magnelli phases formation. Indeed, formation of V_3O_7 impurities in final VO_2 and the changes in the product morphology (nano- and microrods) as a result of oxygen pressure variations [22] support this suggestion. PLD method was also used in the synthesis of doped vanadium dioxide on silicon [23] or quartz [23,24].

Sol-gel method includes the preparation of precursor solution, its transformation into sol, and then into gel due to hydrolysis and condensation, with subsequent aging, drying, and thermal treatment. The production of thin films can occur on the stage of gel formation by placing the inorganic polymer formed in the stage of condensation onto the substrate.

The effect of synthesis conditions on the reaction products is also evident for sol-gel approach, see [25–27].

V_2O_5 reduction on the substrate [28,29] is one of the possible modifications of VO_2 sol-gel synthesis, the initial Magnelli phases can be converted into VO_2(B) and VO_2(M) [29].

Sol-gel technology can also be used to synthesize doped VO_2 thin films on sapphire [30], aluminum [31], silicon [27], or glass [32] substrates.

The obvious advantage of sol-gel method is the high degree of initial components homogeneity.

VO_2 nanofilms are also synthesized by atomic layer deposition. The use of this approach allows to obtain the precise nanoobjects with desired structure through the chemical reaction of functional groups on the matrix surface with the reagents [33–36]. The possibility of Fe and Cr ions introduction into VO_2 is discussed in [36], it is shown that the synergetic effect takes place during doping procedure, it leads to the significant temperature decrease in SMRT phase transition.

Note that some techniques described above were successfully tested for the creation of smart windows based on VO_2 [23,37–38]. These smart windows prevent room temperature increase over the critical value (usually, 29 °C) due to the fact that VO_2 phase transitions prevent IR-emission transmission at higher temperatures.

3. SYNTHESIS OF VO_2 NANOPOWDERS

The main route to VO_2 nanopowders is the hydrothermal synthesis. Its characteristic feature is the possibility of obtaining particles with different morphology mainly due to process temperature and its duration. Hydrothermal synthesis is based on reduction of water-soluble vanadium(V) compounds (preferably, ammonium vanadate or vanadium(V) oxide) at elevated temperatures and pressures in the presence of reductants, preferably, organic acids. The important factor that causes the product morphology in this case is V(V)/reductant ratio. All the authors agree that reaction conditions, synthesis duration, and initial reagents drastically affect VO_2 synthesis.

The typical experiment includes several steps. First, the reactants are mixed using magnetic stirrer until homogeneous suspension or solution is formed. Further, this system is placed into autoclave and treated hydrothermally at the temperatures between 120 and 260 °C for, at least, 12 h. At the final step, the product is separated by centrifugation, washed using water and alcohol, and dried.

The main product formed in hydrothermal synthesis is VO_2(B) that can be converted into VO_2(I) by further heating [39]. Sometimes, other vanadium oxides are also formed as admixtures [40]. The size of obtained particles (nanorods and nanobelts) lies from 20 to 200 nm in width and 1 to 2.5 μm in length [41–44] depending on the synthetic conditions. Hydrothermal method can also provide single crystals composed of 20 nm thick VO_2 nanosheets [45].

So, the factors that influence on VO_2 powder morphology can be conditionally divided onto physical and chemical ones. The chemical factors are: V(V)/reductant molar ratio, reductant's nature, and the presence of modifying agents. The physical factors are interrelated temperature and pressure, as well as process duration.

The most used vanadium-containing initial compounds are ammonium vanadate [40,46] and vanadium pentoxide [47, 48].

The typical reductant is oxalic acid, whereas the vanadium/acid molar ratio lies within the range from 1 to 3. Formic acid [40], aniline [47], hydrazine [39,49], benzylamine [41], and n-butanol [50] were also used. It is noted [40] that other carboxylic acids lead to nanostructures of other vanadium oxides.

The increase in oxalic acid concentration gives rise to enlargement of particles; nanowires or nanobelts convert into nanorods and then into particle array [46,51,52]. The authors of [51] explain these effects by acceleration of V_2O_5 to VO^{2+} reduction due to the increase in acid concentration and the following formation of small-size nanowires. These nanowires were very close to each other, therefore, nanobundles can be formed.

The limited series of modifying agents were suggested for changing product morphology: sulfuric acid [49,53], that probably changes pH value of the initial solution, or octadecylamine [49]. As the amount of octadecylamine increases, nanorods convert into nanospheres. We should note that hydrothermal synthesis with sulfuric acid could be accompanied by the side reaction – reduction of sulfate ion by oxalic acid. This reaction decreases the real reductant/vanadium ratio and, therefore, product morphology is changed.

The study of the interrelation between physical parameters and the product morphology showed [46,50,52] that the duration of process can be diminished in case when the temperature is increased, because the generated high pressure accelerates the reaction. The synthesis with the increased duration (more than 48 hours) permits to obtain well-crystallized micron-sized products. Significant temperature increase (up to 270 °C) together with the increased process duration (from 3 to 24 h) lead to the change in the product structure from VO_2(B) nanobelt to rod-like VO_2(A) and snowflake-like particle VO_2(R); these changes are similar to those occurring lower temperatures [52].

The conditions typical for the hydrothermal synthesis are: the duration between 24 and 48 hours and the temperature ~180 °C.

In addition, core-shell carbon-coated VO_2 microspheres can be obtained by hydrothermal method [54,55]. These microspheres demonstrate good stability in water as well as in organic solvents during cyclization. Other products of hydrothermal treatment are VO_2 nanorods with diameter of ca. 50 nm and length between 300 and 500 nm [53,56]. Authors of [57] describe the hydrothermal synthesis of one-dimensional solid solutions of tungsten-doped VO_2.

Nanoparticles of VO_2 could be obtained hydrothermally by reduction of V_2O_5 in the presence of organic carbon sources [58].

It is suggested to synthesize tungsten-doped VO_2 nanopowders by the thermal reduction of V_2O_5 sol obtained in the presence of tungstic acid by its treatment at 500 °C under nitrogen and NH_3 flow [59].

4. CONCLUSIONS

Vanadium dioxide is a very promising object for the development of smart materials for a wide range of practical applications: from holographic elements to thermochromic coatings.

The possibility to use VO_2 in the specific area depends on the semiconductor-to-metal phase transition characteristics in the certain material. The main parameter that determines the VO_2 properties is its morphology together with particle size and doping. The numerous existing ways for VO_2 synthesis are quite diverse and many variations of dimension distributions, composition, and material structure can be obtained. This raises new ambitious goals for the researchers.

Summarizing the above-mentioned facts, we can state that the morphologic parameters are the main characteristics for possible applications of materials based on VO_2 in certain practical areas. Thus, the enhancement of known synthetic techniques and the development of novel synthesis approaches are very perspective in order to obtain modern products with more complicated compositions and structures.

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REFERENCES

[1] F.J. Morin // *Phys. Rev. Lett.* **3** (1959) 34.
[2] R.M. Wentzcovitch, W. Schulz and P.B. Allen // *Phys. Rev. Lett.* **72** (1994) 3389.
[3] R. Sakuma, T. Miyake and F. Aryasetiawan // *Phys. Rev. B.* **78** (2008) 075106.
[4] C.H. Griffiths and H.K. Eastwood // *J. Appl. Phys.* **45** (1974) 2201.
[5] J. Nag and R.F. Haglund Jr // *J. Phys.: Condens. Matter* **20** (2008) 264016.
[6] D. Vernardou and M.E. Pemble // *Thin Solid Films* **515** (2007) 8768.
[7] Q. Su, C.K. Huang and Y. Wang // *Journal of Alloys and Compounds* **475** (2009) 518.
[8] C.S. Blackman, C. Piccirillo, R. Binions and I.P. Parkin // *Thin Solid Films* **517** (2009) 4565.
[9] P. Kiri, M. Warwick, I. Ridley and R. Binions // *Thin Solid Films* **520** (2011) 1363.
[10] X. Yi, C. Chen and L. Liu // *Infrared Physics & Technology* **44** (2003) 137.
[11] R.A. Aliev and V.A. Klimov // *Solid State Physics* **46** (2004) 515.
[12] M.D. Negra, M. Sambi and G. Granozzi // *Surface Science* **494** (2001) 213.
[13] Atrei, T. Cecconi and B. Cortigian // *Surface Science* **513** (2002) 149.
[14] W. Gao, C.M. Wang and H.Q. Wang // *Surface Science* **559** (2004) 201.
[15] G. Beydaghyan, V. Basque and P.V. Ashrit // *Thin Solid Films* **522 (**2012) 204.
[16] Y. Cui, X. Wang and Y. Zhou // *Journal of Crystal Growth* **338** (2012) 96.
[17] S. Saitzek, F. Guinneton and G. Guirleo // *Thin Solid Films* **516 (**2008) 891.
[18] Y. Muraoka, Y. Ueda and Z. Hiroi // *Journal of Physics and Chemistry of Solids* **63** (2002) 965.
[19] K. Okimura and N. Kubo // *Thin Solid Films* **515** (2007) 4992.
[20] J.B. Kana Kana, J.M. Ndjaka and B.D. Ngoma // *Optical Materials* **32** (2010) 739.
[21] J. Li and J. Dho // *Crystal Growth* **312** (2010) 3287.
[22] N. Rama and M.S. Ramachandra Rao // *Solid State Communications* **150** (2010) 1041.
[23] B. Chen, D. Yang, P. A. Charpentier and M. Zeman // *Solar Cells* **93** (2009) 1550.
[24] Kaushal, N. Choudhary, N. Kaur and D. Kaur // *Applied Surface Science* **257** (2011) 8937.
[25] J. Wu, W. Huang and Q. Shi // *Applied Surface Science* **268** (2013) 556.
[26] K.R. Speck, H.S.-W. Hu, M.E. Sherwin and R.S. Potember // *Thin Solid Films* **165** (1988) 317.

[27] M. Pan, H. Zhong and S. Wang // *Journal of Crystal Growth* **265** (2004) 121.
[28] D. Yin, N. Xu, J. Zhang and X. Zheng // *Materials Research Bulletin* **31** (1996) 335.
[29] Y. Ningyi, L. Jinhua and L. Chenglu // *Applied Surface Science* **191** (2002) 176.
[30] B.G. Chae and H.T. Kim // *Physica B* **405** (2010) 663.
[31] J.-H. Cho and Y.-J. Byun// *Ceramics International* **38** (2012) S589.
[32] T.J. Hanlon, J.A. Coath and M.A. Richardson // *Thin Solid Films* **436** (2003) 269.
[33] G. Rampelberg and M. Schaeker // *Appl. Phys. Lett.* **98** (2011) 162902.
[34] P. Dagur, A.U. Mane and S.A. Shivashankar // *Journal of Crystal Growth* **275** (2005) e1223.
[35] O. Osmolowskaya and and V. Smirnov // *Rev. Adv. Mat. Sci.* **27** (2011) 184.
[36] D.V. Nazarov, O.M. Osmolovskaya, N.P. Bobrysheva, V.M. Smirnov and I.V. Murin // *Nanotechnologies in Russia* **7** (2012) 641.
[37] P. Kiri, M. Warwick, I. Ridley and R. Binions // *Thin Solid Films* **520** (2011) 1363.
[38] Z. Huang and S. Chen // *Thin Solid Films* **519** (2011) 4246.
[39] Z. Gui and R. Fan // *J. Solid State Chemistry* **157** (2001) 250.
[40] K.C. Kam and A.K. Cheetham // *Materials Research Bulletin* **41** (2006) 1015.
[41] F. Sediri and N. Gharbi // *Materials Science and Engineering: B* **139** (2007) 114.
[42] X. Liu and G. Xie // *Materials Letter* **62** (2008) 1878.
[43] K.F. Zhang and S.J. Bao // *Materials Reseach Bulletin* **41** (2006) 1985.
[44] W. Chen and J. Peng // *Solid State Communications* **132** (2004) 513.
[45] M. Wei and Z.M. Qi // *Journal of crystal growth* **296** (2006) 1.
[46] W. Jiang and J. Ni // *Applied Surface Science* **257** (2011) 3253.
[47] F. Sediri, F. Touati and N. Gharbi // *Materials Science and Engineering B* **129** (2006) 251.
[48] N. Ganganagappa and A. Siddaramanna // *Materials Characterization* **68** (2012) 58.
[49] R. Li and C.-Y. Liu. // *Materials Research Bulletin* **45** (2010) 688.
[50] X. Li and X. Chen // *Journal of Crystal Growth* **309** (2007) 43.
[51] H. Yin and K. Yu // *Applied Surface Science* **257** (2011) 8840.
[52] S. Ji, F. Zhang and P. Jin // *Journal of Solid State Chemistry* **184** (2011) 2285.
[53] S. Ji and Y. Zhao // *Journal of Crystal Growth* **312** (2010) 282.
[54] F. Wang, Y. Liu and C. Liu // *Electrochimica Acta* **55** (2010) 2662.
[55] C. Nethravathi and B. Viswanath// *Carbon* **50** (2012) 4839.
[56] J.Q. Fernando and O.P. Heloise // *Materials Research Bulletin* **45** (2010) 892.
[57] J. Li, C. Liu and L. Mao // *Journal of Solid State Chemistry* **182** (2009) 2835.
[58] F. Wang, Y. Liu and C. Liu // *Journal of Solid State Chemistry* **182** (2009) 3249.
[59] Z. Peng and Y. Wang // *Journal of Alloys and Compounds* **480** (2009) 537.