Oxygen-dependent formation of VO_2 Thin Films by Metalorganic Aerosol Deposition

Belenchuk A., Shapoval O., Zasavitsky E.
IIEN, Academy of Sciences of Moldova,
Chișinău, Republic of Moldova

Vatavu S., Chirita A.
Physics department, State University of Moldova,
Chișinău, Republic of Moldova

Moshnyaga V.
I. Physikalisches Institut, University of Göttingen
Göttingen, Germany

***Abstract*—We report on the growth and properties of vanadium dioxide (VO_2) on amorphous and oriented substrates by the low-cost and industry-oriented method of metalorganic aerosol deposition (MAD). X-ray diffraction and temperature-dependent Raman spectroscopy confirm formation of single phase tin films. Abrupt change of resistance by 5×10^3 times and steep drop of infrared transmission from 49 to 10% at 1700 nm pave the way for application of MAD technique in fabrication of VO_2-based optoelectronic and thermochromic devices, such as "smart windows".**

***Index Terms*—VO_2 thin films, metalorganic aerosol deposition, surface morphology, crystal structure, Raman spectroscopy, resistance switching, optical transmittance.**

I. Introduction

Vanadium dioxide is a strongly correlated material that possesses a first order reversible semiconductor to metal transition (SMT) at 68°C accompanied with transformation from tetragonal to monoclinic structure. Sharp and ultrafast changes in electrical and optical properties make VO_2 a very promising material for diverse applications including optical modulators, infrared bolometers and "smart windows" for energy-efficient buildings [1].

A variable valence of vanadium complicates synthesis of a pure single-phase VO_2 material, since depending on conditions of oxidation synthesis of different vanadium oxides (VO, V_2O_3, V_2O_5 etc.) are possible. Nevertheless, by precise control of oxidation level the most physical and chemical methods of thin film deposition have been successfully applied to the VO_2 thin film preparation. However, in the case of a high-throughput manufacturing, which is requested by "smart windows" for building glazing, an atmospheric pressure chemical vapour deposition has great benefits over the other techniques due to lack of vacuum, low-cost and compatibility with the on-line float-glass production.

Here we report on the oxygen-dependent optimization of the metalorganic aerosol deposition (MAD) technique [2], which is a variation of atmospheric pressure CVD method, for fabrication of pure single-phase VO2 thin films.

II. Experiment

The precursors V(acetylacetonate)$_3$ or VO(acetylacetonate)$_2$ were dissolved in dimethylformamide to a concentration of 0.08 mol/l. To prepare thin films of vanadium oxides the solution was pneumatically sprayed using a compressed gas, a mixture of Ar and O_2, on Al_2O_3(0001) or SiO_2/Si(111) substrates heated to ~470°C with deposition rate fixed at 1 nm/s. The oxygen content (O_2 to Ar ratio in the gas mixture) was the only variable parameter, all other thermodynamic and kinetic parameters were constant. The thin film structure and morphology were characterized by x-ray diffraction, scanning electron microscopy (SEM) and atomic force microscopy (AFM). Temperature-controlled Raman spectroscopy was used for detailed characterization of the material structure and the phase transition. Temperature-dependent resistivity and optical transmission below and above SMT were measured to establish influence of the O_2-content in the gas mixture on the amplitude, sharpness and position of the SMT as well as to estimate perspectives for fabrication devices on the basis of MAD-prepared VO_2 films.

III. Results

Depositions in a pure O_2 atmosphere result in formation of material that possesses a lot of small peaks on the X-ray diffraction spectra, indicating thus formation of mixture of various vanadium oxides. The material has a rather low resistivity with a weak temperature dependence of resistance that is without evident SMT. However, after differentiation of the R(T) curve a small singularity was appeared at about 340K, confirming presence of a small fraction of VO_2 phase in the films. From the other side, in a pure Ar atmosphere deposition of films results in formation of material possessed even lower resistance, but without any singularity at the vicinity of SMT temperature and without any diffraction peaks.

Step-by-step adjustment of the gas mixture allows us to determine an optimal content of oxygen. We established that content of oxygen equal to 0.3÷0.4% is an optimal for

synthesis of a pure single-phase VO_2 by MAD technique with the specified above technological conditions.

Analysis of surface morphology shows that films deposited at optimal O_2-content are continuous and composed of homogeneous crystalline grains with irregular shapes. Average size of crystallites and surface roughness are considerably different for films grown on amorphous and single crystalline substrates. Surface morphologies obtained by SEM on the typical films grown on amorphous SiO_2/Si(111) and single-crystal Al_2O_3(0001) substrates are shown on Fig. 1 and 2, respectively. Lateral dimensions of VO_2 nanocrystals are respectively equal to 80÷150 and 40÷70 nm for polycrystalline and oriented growth. As a result surface root mean square roughness values, which were determined by AFM, are significantly diverse with the average values equal respectively to 10.4 and 4.1 nm for the presented on Fig. 1 and 2 samples.

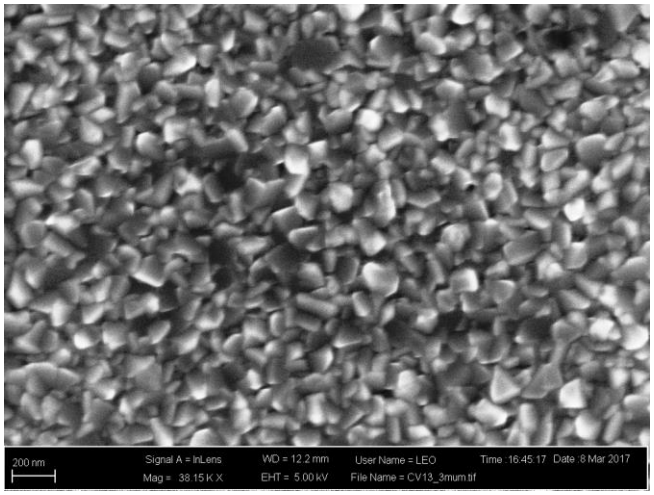

Fig. 1. SEM image of 71-nm-thick VO_2 film deposited on SiO_2/Si(111) substrate.

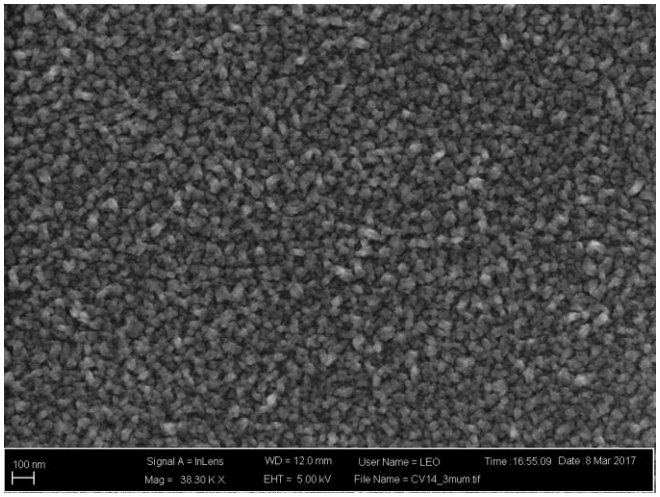

Fig. 2. SEM image of 82-nm-thick VO_2 film grown on Al_2O_3(0001) substrate.

The film thickness was determined by the interference fringes on a small-angle x-ray scattering curves. In the case of deposition on amorphous SiO_2/Si(111) a very rough film surface impedes formation of regular fringes. But oriented growth on single crystal Al_2O_3(0001) substrate with smaller grain size and smaller roughness forms clear fringes and allows to determine of film thickness. Therefore, to determine film thickness on amorphous substrate we used simultaneous deposition on Al_2O_3(0001) substrate as a reference sample.

At optimal O_2-content in the gas mixture all X-ray diffraction 2θ–ω scans reveal diffraction peaks inherent to the structure of monoclinic VO_2 only. X-ray diffraction spectra of O_2-optimized VO_2 thin films are shown on Fig.3 and Fig.4 for SiO_2/Si(111) and Al_2O_3(0001) substrates, respectively. For the deposition on Al_2O_3(0001) substrate the scan contains two well-distinguished peaks (002) and (004) only, indicating thus formation of a single (001)-oriented VO_2 film.

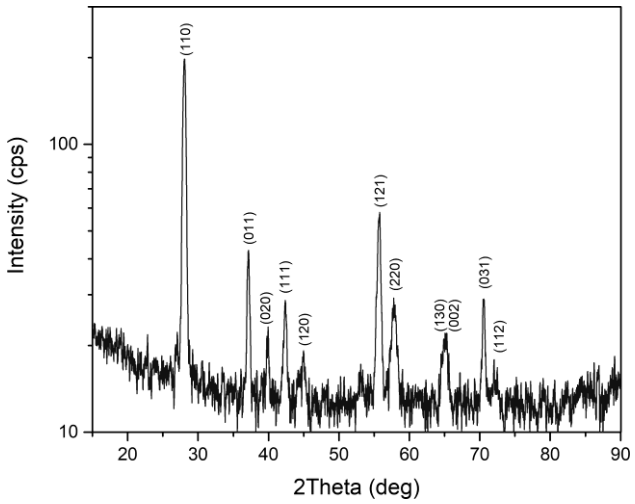

Fig. 3. X-ray diffraction scan for VO_2 film deposited on SiO_2/Si(111) substrate.

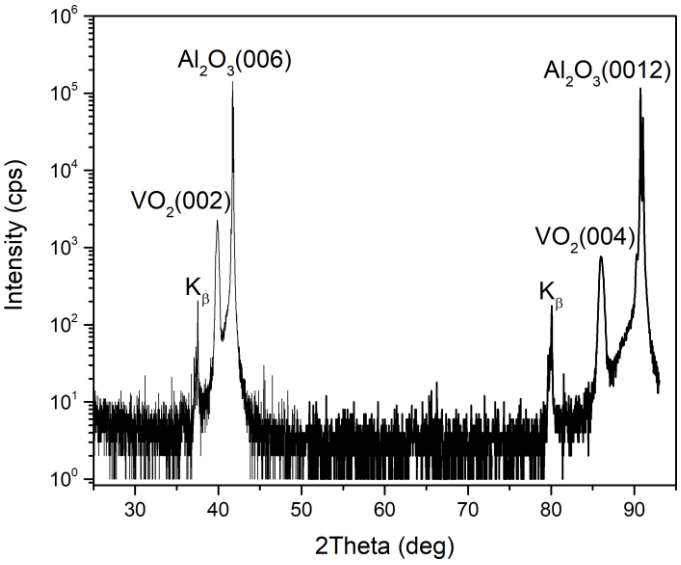

Fig. 4. X-ray diffraction scan for VO_2 film grown on Al_2O_3(0001) substrate.

In addition to analysis of structure with X-ray diffraction, to examine SMT in VO_2 we applied temperature-dependent Raman spectroscopy, which is exceptionally sensitive to strain induced lattice distortions as well as to a

small change of symmetry between VO_2 polymorphs. A typical Raman spectrum that was obtained on a polycrystalline VO_2 film grown at the optimal conditions is shown on Fig. 5 (300K). The spectrum contains peaks of the characteristic vibration modes from the monoclinic VO_2 only. The most intensive Raman peaks at 148, 194, 225, 313, 396 and 613 cm^{-1} can be identified as the A_g vibration modes. All detected peaks are well coincided with the previously published values for the monoclinic structure of VO_2 [3], confirming thus the absence of vibration shift due to non-stoichiometry of material. Any peaks corresponded to other vanadium oxide phases, including the most stable V_2O_5, were not observed. Note that the most intensive off-scaled peak on Fig. 5, which is situated at 520 cm^{-1}, corresponds to the single crystal Si substrate.

The spectra on Fig. 5 indicate presence of a small fraction of the second monoclinic phase (M2) with characteristic line situated at ~660 cm^{-1}. M2 phase develops a small feature at the slope of big peak at 613 cm^{-1}, which relates to the principal M1 monoclinic phase. It is well-known that uniaxial stress in VO_2 leads to the formation of M2 phase at the transition from high-temperature rutile and low-temperature M1 structures. Only half of the vanadium ions in the M2 phase participate in dimerization. Therefore, the emergence of the M2 phase as an intermediate state between the M1 and rutile phases was proposed to be universal [4]. Moreover, the M1 phase can be interpreted as a superposition of two M2 phases. While the origin of M2 phase formation is still under debate, presented here Raman spectra confirm the importance of the M2 phase in the SMT of VO_2. It was early established that in polycrystalline VO_2 films the tensile stress along [011] M1 direction favors formation of the M2 phase [5]. We can thus conclude that MAD-prepared VO_2 films seem to be exposed to stress in the same direction due to probably a relatively large mismatch of thermal coefficients between Si substrate and VO_2 film.

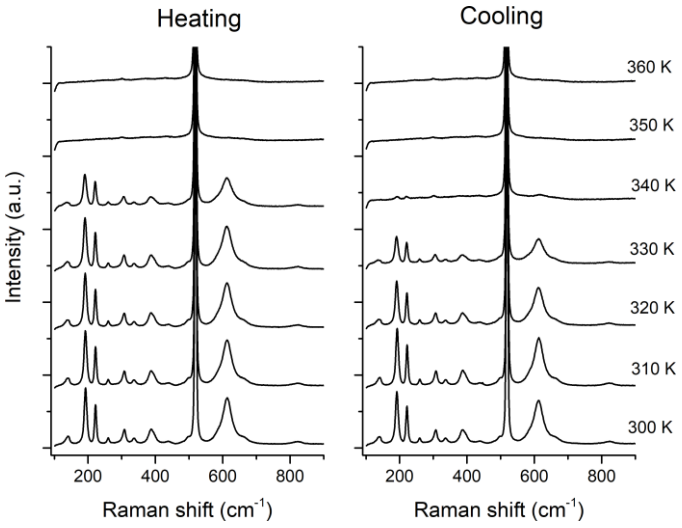

Fig. 5. Raman spectrum evolution with temperature for VO_2 film deposited on SiO_2/Si(111) substrate.

Raman spectroscopy measurements were also performed at several fixed temperatures during heating and cooling of samples over the VO_2 phase transition. The evolution of Raman peaks for the VO_2 films during the scan of temperature is presented on Fig. 5. On heating the sample the Raman peaks of monoclinic VO_2 becomes gradually less intensive as the temperature increases and approaches to the phase transition point. Above the transition temperature, the Raman peaks are completely disappeared. This effect indicates that VO_2 film undergoes the SMT with simultaneous transition between the monoclinic and tetragonal (rutile) structures. However, the high-temperature VO_2 phase has no any peaks because of the metallic behavior of material and a well-known effect of screening lattice vibrations by free electrons.

Measurements of resistance allow us to determine more exactly parameters of the phase transition in MAD-prepared VO_2. A typical curve of temperature-dependent resistance for the oriented film is shown on Fig. 6. The sharpness of transition was determined by calculation quantity of thermal coefficient of resistance, TCR=(1/R)(dR/dT). Positions of transitions at heating and cooling and the hysteresis width are well satisfied to the pure vanadium dioxide phase, and achievement of resistance ratio by 5×10^3 times indicates formation of a high quality VO_2.

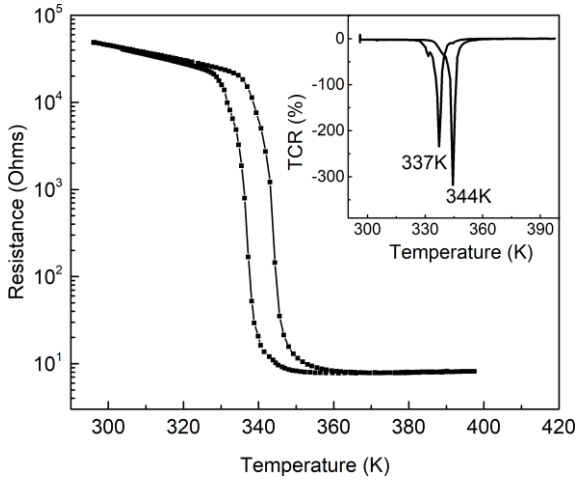

Fig. 6. Temperature dependence of the resistance for VO_2 film grown on Al_2O_3(0001) substrate. The inset shows thermal coefficient of resistance, TCR=100%×(1/R)/(dR/dT).

The resistivity ratio for polycrystalline VO_2 thin film is slightly smaller (~1.5×10^3), and sharpness of the transition is also smaller than for the oriented films due a well-known effect of scattering curriers at grain boundaries in metallic state above the transition temperature. But the transition temperature and hysteresis width are well matched with the same values for the oriented films, evidencing thus a high quality of material that composes individual crystal grains of the polycrystalline VO_2 films.

In order to simulate correctly operation of "smart windows", the optical transmittance of films was measured with an appropriate monochromator. Our choice of the monochromator instead of spectrophotometer is determined by possibility to illuminate sample with a total wavelength

spectrum, while spectrophotometer utilizes for illumination a single wavelength only. That is utilization of the monochromator reproduces more correctly operation of "smart windows". Increasing of sample temperature due to illumination by the whole spectrum was preliminary calibrated and taken into account for subsequent measurements. Typical optical transmittance spectra from 400 nm to 1800 nm obtained below and above the SMT are presented on Fig. 7. It is clear that the film of 82-nm-thick VO_2, which was grown at optimal O_2-content, exhibits remarkable switching of the near infrared transmittance, preserving at the same time a rather high luminous transmittance independent to the temperature. The modulation efficiency at 1700 nm reaches value of 81%. The luminous transmittance approaches values of 45 and 37% for semiconductive and metallic states, respectively. The superior thermochromic performance is also confirmed formation of a high quality VO_2 thin film.

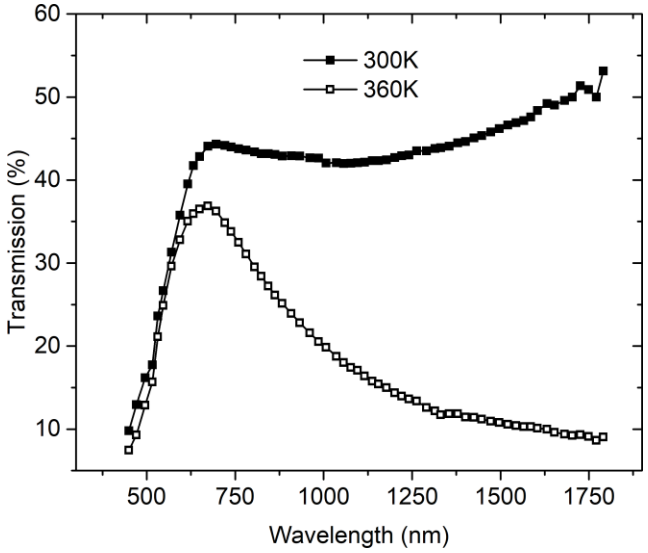

Fig. 7. Transmittance vs wavelength at temperatures below and above the SMT for film grown Al_2O_3(0001) substrate.

IV. Conclusion

Analysis of structure and surface morphology, electrical and optical characterizations of the films confirm formation of single-phase vanadium dioxide by oxygen controlled MAD technique. The optimized films possess the phase transition temperature, hysteresis width, and amplitudes of the optical and electrical modulations that are well corresponded to a high quality VO_2 thin films. The obtained results open way for further implementation of MAD technique to the thermochromic "smart windows" fabrication.

Acknowledgment

The authors acknowledge financial support by the STCU project #6133 and the Deutsche Forschungsgemeinschaft (DFG) via SFB 1073 (TP B04, B01).

References

[1] Mickael E. A. Warwick, Russell Binions, "Advances in thermochromic vanadium dioxide films", J. Mater. Chem. A, vol. 2, pp. 3275–3292, March 2014.

[2] V. Moshnyaga, et al., "Preparation of rare-earth manganite-oxide thin films by metalorganic aerosol deposition technique" Appl. Phys. Lett. 74, pp. 2842–2844, May 1999.

[3] Keisuke Shibuya, Jun'ya Tsutsumi, Tatsuo Hasegawa, and Akihito Sawa, "Fabrication and Raman scattering study of epitaxial VO_2 films on MgF_2 (001) substrates", Appl. Phys. Lett. 103, pp. 021604-4, July 2013.

[4] Joanna M. Atkin, et al., "Strain and temperature dependence of the insulating phases of VO_2 near the metal-insulator transition", Phys. Rev. B 85, pp. 0201014, January 2012.

[5] Kunio Okimura,et al., "Temperature-dependent Raman and ultraviolet photoelectron spectroscopy studies on phase transition behavior of VO_2 films with M1 and M2 phases", J. Appl. Phys. 115, pp. 1535016, April 2014.