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Effect of MIT in epitaxial VO_2 films on THz transmittance

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The development of THz technologies (communication, imaging, spectroscopy etc.) requires the design of materials for high-speed modulation of radiation in THz range. For such applications, the thin films based on oxides showed a metal-insulator transition (MIT) are interesting due to large different of optical transmittance before and after critical point. Among the oxide materials with MIT vanadium dioxide, which has a transition temperature the closest to the room temperature (68°C for bulk samples), is of particular interest, with the MIT characterized by a record speed (<1 ps) and a large amplitude (a change in the conductivity is 10^5 times for single crystals). It is known that the MIT transition in VO_2 is accompanied by a first-order phase transition, while the crystalline structure from the monoclinic (crystal type MoO_2) with the properties of the semiconductor transforms into a tetragonal (rutile type) with metallic conductivity. The electronic transition in the vanadium dioxide can be caused by the temperature, the electric field and laser radiation. A set of these unique properties makes vanadium dioxide a promising key component of optoelectronic devices (switches, modulators, lenses, etc.) for the THz range controlled by thermal action, electric voltage or laser pulse.

Recently the efforts of numerous researches were directed to the vanadium dioxide in the form of thin epitaxial films of thickness (100-500 nm) on optically transparent single-crystal substrates (Al_2O_3, TiO_2). The epitaxial VO_2 films exhibit the sharp transition with an amplitude changes in conductivity up to four orders of magnitude and showed above 90% change of THz transmission.

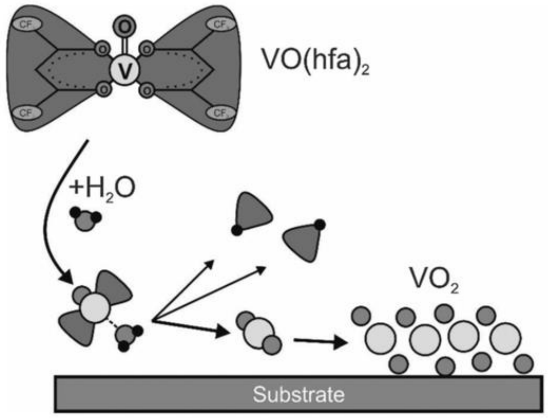

Fig. 1. The scheme of reaction between $VO(hfa)_2$ molecule and water resulted to formation of VO_2.

The properties of vanadium dioxide are very sensitive to the concentration of defects, morphology, contact between crystallites, impurities of other elements. The synthesis of epitaxial films of vanadium dioxide, extremely limited by a narrow region of homogeneity and a high sensitivity to the partial pressure of oxygen, is a complex problem, which resulted in a low reproducibility of the composition and properties of films obtained in different scientific groups.

The method of chemical vapor deposition is a promising method for the production (on an industrial scale) of vanadium dioxide films demonstrating the properties of an optical switch in the THz range, however, provided a simple and effective process for obtaining high-quality samples that are not contaminated with impurity phases. In the case of materials sensitive to the oxygen partial pressure, the use of water vapor for destruction of the vanadium containing molecules makes possible to obtain stoichiometric VO_2 due to stabilization of vanadium oxidation state +4 and to carry out the deposition process at low temperatures (> 350°C) without carbon contamination of the film. In our work we performed the deposition of epitaxial $(001)VO_2$ films on r-Al_2O_3 substrates (diameter 1-3 inches) by gas-phase reaction between vapors of vanadyl diketonates $VO(dik)_2$ (dik^- = $acac^-$, thd^-, hfa^-) and water in argon atmosphere at temperature range 350-600°C.

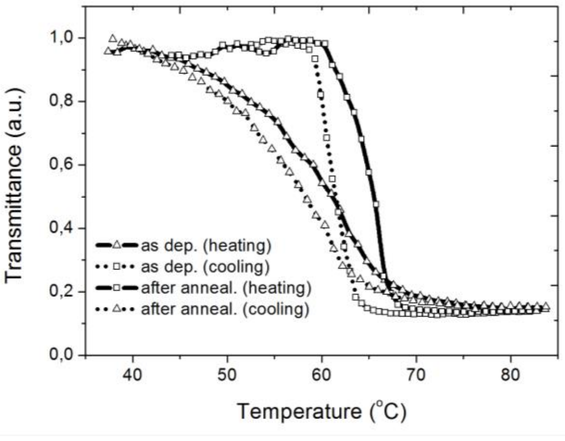

Fig. 2. The THz transmittance of VO_2/r-Al_2O_3 (as deposited and after annealing) films at different temperature.

Among the many factors that influences on the nature of the MIT in vanadium dioxide, the film microstructure plays one the most important role. Fine-grained films that have a large number of partially oxidized grain boundaries show a diffuse hysteresis loop and a smaller amplitude of the resistance change. The increase of the grain size can be achieved either by increasing the substrate temperature, or by using an additional heat treatment. In the first case, the formation of a partially oxidized grain surface is not prevented, whereas additional annealing successfully solves this problem due to the peritectic decomposition of the oxidized phases occurs to VO_2 and trace amounts of the melting phases promoting recrystallization process. The samples obtained by MOCVD process were annealed under conditions of controlled oxygen partial pressure at temperature range 550-650^{o}C resulted in increasing of grain size, changing of morphology, electrical and optical properties. It was investigated the films composition, structure, morphology and physical properties.

Measurements of the THz transmission as a function of temperature were carried out on a pulsed THz spectrometer. It was demonstrated the effect of films synthesis on the contrast of transmission in the dielectric and conducting state. The shape of the hysteresis loop differs from the resistance curve and is somewhat shifted downward in temperature associated with percolation of conductive grains into the insulation matrix. For large-scale substrates the maps of THz amplitude change were analyzed.

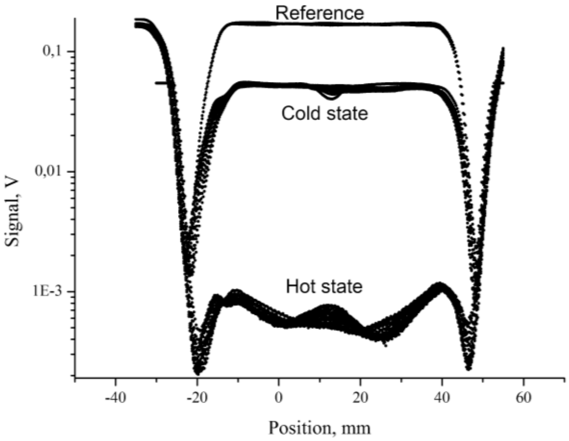

Fig. 3. The THz transmittance of 3-inch VO_2 films on r-Al_2O_3 at different position from the center (10 mm).

Moreover most of practical applications require non-trivial shape and design of functional optical elements, then it is important to have possibility to realize the chemical lithography operations that accurately was demonstrated in this work.

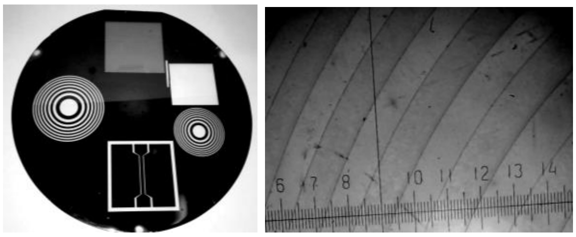

Fig. 4. The different patterns on 3-inch VO_2 film/Al_2O_3 obtained by photolitographic etching process.

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