



## Synchrotron analysis of structure transformations in V and V/Ag thin films



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### ABSTRACT

Crystal structure transformations in V(25 nm)/SiO<sub>2</sub>(001) and V(25 nm)/Ag(25 nm)/SiO<sub>2</sub>(001) thin films during annealing in vacuum of 10<sup>-3</sup> Pa in the temperature range from 400 °C to 600 °C have been investigated by synchrotron X-ray powder diffraction. Crystal lattice parameters of VO<sub>x</sub> phase were evaluated for all transformations stages as well as its tetragonality degree. Additional techniques such as *in-situ* electron diffraction, secondary ion mass-spectrometry and transmission electron microscopy have been applied as well. Introduction of the Ag layer affects the V film structure and its oxidation property during annealing. The body-centered monoclinic (bcm) lattice forms in V films after annealing. On the other hand, presence of the Ag layer leads to formation of the body-centered tetragonal (bct) structure during annealing at the same temperature. Ag suppresses oxygen incorporation into the film during annealing due to its diffusion into V grain boundaries and following diffusion induced grain boundary migration, leading to decrease of vanadium grains size. Mentioned above structural changes have not been detected for samples annealed in a vacuum of 10<sup>-7</sup> Pa in the same temperature range.

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### 1. Introduction

Because of "metal-insulator" phase transition, vanadium oxides thin films are considered as prospective materials for sensors electronics application. That is why most of existing investigations are directed to divergent aspects of vanadium oxides formation and application [1–3].

For such potential applications as adhesive sub layers, diffusion barriers or protective coatings V thin films attract huge interest as well. Such films could be obtained by magnetron sputtering [4] or electron beam evaporation in ultra-high vacuum [5].

However, high affinity of V with O<sub>2</sub> results in the problems of its interaction with substrate [6] and with oxygen impurities from a residual atmosphere [7]. Such interaction could significantly affect the device formation and degrade fabrication reproducibility. First

of all, this problem belongs to electrical [8] and optical [9] properties, which are investigated in great details.

Oxidation processes of V thin films are also important in connection to their magnetic properties. Magnetism of transition metals surfaces could be used for creation of a magneto-optical storage medium with an ultra-high recording density. Paramagnetic vanadium could come to a ferromagnetic state in the frames of 2 atomic layers on Ag(100) or Fe(100) surfaces [10]. However, magnetic moments are very sensitive to the presence of oxygen impurities [11].

There are more than 20 compounds in V-O system [12] and most of them have stoichiometric structures with oxygen concentrations higher than 60 at.%. These compounds have been well investigated [13–15].

On the other hand, vanadium oxides with an oxygen concentration <60 at. % are not stoichiometric compounds. Formation features of such compounds (especially in thin films) and ranges of their homogeneity have not been investigated so far. Existence of oxygen solid solution in V ( $\beta$  phase) with a maximum solubility in bulk material from 4 at. % (room temperature) up to 17 at.% (1938 K)

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should be taken into account. During solid solution formation oxygen atoms are located in V lattice octahedral pores, leading to V body-centered cubic (bcc) crystal structure transformation into body-centered tetragonal (bct) one [16].

In this paper we have investigated formation of vanadium suboxides with an oxygen concentration <50 at. % in thin films, obtained in ultra-high vacuum. In order to investigate early stages of oxidation process we applied annealing in a low vacuum of  $10^{-3}$  Pa instead of annealing in an oxygen atmosphere which is commonly used for stoichiometric oxides formation.

Ag layer was deposited onto a substrate in order to prevent its interaction with V [17–19]. We also expected that introducing of Ag layer could be useful in terms of oxidation rate control and improvement of electrical and physical properties of the films. Earlier it was shown that increase of Ag concentration in catalysts lowers a vanadium oxides reduction temperature [20]. Positive Ag effect was also reported for application of V-O thin films in lithium-ion batteries [21]. Possibility of batteries cycle stability drastic improvement was shown because of the high capacity and conductivity of Ag-V<sub>2</sub>O<sub>5</sub> cathodes. Mixture of Ag atoms and a silver oxide could be incorporated into V<sub>2</sub>O<sub>5</sub> lattice [22].

Mechanisms of the diffusion interaction between Ag and V as well as between Ag and vanadium oxides in thin films were not investigated so far.

The goal of the present work is to determine structural transformation features in V(25 nm)/SiO<sub>2</sub>(001) and V(25 nm)/Ag(25 nm)/SiO<sub>2</sub>(001) thin films during annealing in vacuum of  $10^{-3}$  Pa in the temperature range 400 °C - 600 °C. Mechanisms of the diffusion interaction between Ag and V and its oxides were also analyzed in order to investigate the role of the Ag additional layer on the V films oxidation.

## 2. Materials and methods

25 nm-thick V thin films and bi-layered stacks of V(25 nm)/Ag(25 nm) were obtained by electron beam evaporation onto SiO<sub>2</sub>(001) single crystal substrates at room temperature in an ultra-high vacuum chamber ( $10^{-7}$  Pa). V (99.7%) was deposited from a rod-form target and Ag (99.99%) from a molybdenum crucible. A distance between the target and the substrate was adjusted to 150 mm. A duration was 36 and 20 min for V and Ag deposition, respectively. Deposition rates were evaluated by profilometer measurements, using the Dektak 200-Si device. Films were also deposited onto NaCl(100) substrates for transmission electron microscopy and *in-situ* electron diffraction measurements, where the films were separated from the substrates.

Deposited films were post-annealed for 15 min in high ( $10^{-7}$  Pa) and low ( $10^{-3}$  Pa) vacuum at 400 °C, 500 °C, and 600 °C.

For the *in-situ* electron diffraction measurements in transmission mode, high voltage of 75 kV was applied. In these measurements samples were annealed up to 600 °C in vacuum ( $10^{-3}$  Pa) with a constant heating rate of 1.2 °C/s.

Structural properties of the films were determined by grazing-incidence wide-angle X-ray scattering (GIWAXS) method, using the RIKEN Materials Science Beamline BL44B2 [23,24]. It should be noted that positions of diffraction peak from a single crystalline SiO<sub>2</sub>(001) substrate and of V 220 peak were too close to be easily resolved using traditional geometry of X-ray analysis. GIWAXS method with application of a 2D-detector allowed us to resolve ring patterns from polycrystalline V and point peak from the single crystalline substrate. Moreover, vanadium oxides VO as well as silver have the face centered cubic (fcc) structure with lattice constant of 4.06 Å, resulting in very close angular positions of the corresponding 111 peaks. Angle position difference between those peaks is less than 0.2°, leading to peaks overlapping and difficulties

in their resolving. These problems were resolved by using both high energy monochromatic X-rays and GIWAXS geometry. The samples were set into the Debye-Scherrer camera with a radius of 286.48 mm. The beam grazing angle was 0.5°. The camera was equipped with an image plate detector (400 × 200 mm). Measurements were carried out in the range from 2° to 78° with a 2θ step of 0.01°. The vertical and horizontal beam sizes were 0.01 mm and 3.0 mm, respectively. The incident wavelength was 1.08 Å, which was calibrated using a standard reference material CeO<sub>2</sub> (SRM 674b; National Institute of Standards & Technology, USA). In order to obtain precise lattice constants, higher-angle Bragg peaks (68–148°) were used for calculations. The errors of lattice constants were estimated to be approximately 0.01 Å by measuring a sintered alumina disk (SRM 1976b; National Institute of Standards & Technology, USA). Calculation of the lattice parameters and peaks identification were performed, using “CrystalDiffract” software.

Microstructure investigations of as-deposited and post-annealed samples were done by transmission electron microscopy (TEM) with accelerating voltage 100 kV (ПЭМ-У).

Films chemical depth profiling was done by secondary ions mass-spectrometry. Advantages of this method for thin films investigations were well described in Refs. [25,26]. Argon ions with energy of 5 KeV were applied as a primary beam. Current of ion beam discharge was 0.4 mA and current of primary beam was 15 μA (calculated current density – 2.5 μA/mm<sup>2</sup>). Ta masks with a thickness of 0.1 mm and a hole in diameter <1 mm were used in order to increase depth resolution. Analysis of the results was done using Spectrum Recorder software.

## 3. Results and discussion

Temperature intervals of phase transformations in V and V/Ag thin films were determined by *in-situ* electron diffraction during annealing at temperatures up to 600 °C in a vacuum of  $10^{-3}$  Pa. Figs. 1 and 2 show electron diffraction patterns for respective temperatures.

There are peaks just from Ag and V on the electron diffraction patterns from as-deposited V/Ag bi-layered stack. Oxide phases were not detected (Fig. 1a). Annealing at 400 °C leads to changes in V layer crystal structure, resulting in broadening of the 011 and 002 peaks and their shift to the lower angles side (Fig. 1b). We assumed that broadening of the 011 peak corresponds to formation of (011)+(110) doublet because of tetragonal lattice formation from the initial body centered cubic (bcc) one. 110 peak disappears after reaching the temperature of 550 °C (Fig. 1c). Following annealing up to 600 °C results in disappearance of 011 peak as well (Fig. 1d). This indicates the formation of the VO phase which has a fcc structure.

Similar measurements of V thin films without Ag layer were carried out (Fig. 2). Diffraction peaks were detected from the (011), (002), (112), (022), (013) and (222) lattice planes indicating bcc V structure (Fig. 2a). Broadening of the 011 peak was detected during annealing at 400 °C, corresponding to the beginning of lattice distortion and formation of the 011 + 110 doublet peaks (Fig. 2b). Formation of vanadium (002)+(200) and (112)+(211) doublets was detected as well. The next increase of annealing temperature up to 600 °C leads to disappearance of the 200 and 211 peaks (Fig. 2c and d). At the same time, the 011 + 110 doublet peaks were observed with a shift of the 011 peak toward the lower angle side, indicating the increase of newly formed lattice tetragonality degree.

It was concluded that the Ag layer significantly affects the transformations of the V crystal structure during annealing in a vacuum of  $10^{-3}$  Pa. This is manifested in an increase of the tetragonality degree of V thin film without an Ag sublayer comparing to V/Ag bi-layers.

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