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GROWTH MECHANISM OF NANODIMENSIONAL VANADIUM DIOXIDE ON SILICON SURFACE OBTAINED BY ML-ALD METHOD

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Abstract. Vanadium dioxide nanostructures on silicon were synthesized on silica surface by method molecular - layering atomic layer deposition (ML-ALD). Based on the X-ray diffraction and AFM study, we showed that the structure and morphology of nanosized vanadium dioxide depends on the number of synthesis cycles. The formation scheme for ML-ALD-synthesized vanadium dioxide nanolayers of the definite thickness on silicon surface is proposed. By using X-ray diffraction, spontaneous crystallization effect was discovered for amorphous vanadium dioxide layer on silicon surface. All crystallites are oriented along the support surface. While increasing number of ML-ALD cycles, the crystallites with more symmetrical lattice are formed. So, 20 cycles of ML-ALD in combination with higher treatment temperature promote change in surface relief of vanadium dioxide.

1. INTRODUCTION

For many years, researchers are interested in ability of vanadium dioxide (VO_2) to undergo reversible structural transformations. These transformations are temperature-dependent and are accompanied by semiconductor-metal phase transition (SMPT). SMPT for bulk VO_2 occurs at 340K. [1,2]. This transition causes drastic changes in physical and chemical properties of the substance.

It is known that SMPT characteristics are greatly influenced by VO_2 particle size and intergrain boundaries. It was shown that transition characteristics are influenced by monolithic support in some ranges due to changes in VO_2 microlayers morphology.

To the moment, there is no doubt that the dependence exists between physical and chemical properties of VO_2 microlayers and their morphology and structure. As a result of synthesis of microlayers on different matrix surfaces by a variety of methods, the products with different properties are formed [3-6].

Therefore, studies of nanosize effects must be performed taking into account the morphology of product.

We have shown recently that for ML-ALD-grown nanosized VO_2 on dispersed silica, SMPT temperature is decreased to 200K [6]. ML-ALD method [6] provides the possibility to synthesize nanostructures VO_2 with the minimal size of ca. 0.3 nm. The subsequent growth leads to the series of the samples of different nanosize that allows investigating relation between size and SMPT characteristics.

Based on the above, we aimed to study herein the dependence between morphology and phase composition of the samples and the number of ML-ALD cycles and subsequent thermal treatment conditions (Table 1).

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Table 1. ALD cycles number and thermal treatment temperature for studied samples.

Sample No.	ALD cycles number	Thermal treatment temperature, ºC
0	Single crystal silicon surface prepared for synthesis	
1	1	–
2	5	–
3	10	–
4	20	–
4.1	20	350
4.2	20	400
4.3	20	450
5	40	–
6	80	–

2. EXPERIMENTAL

The synthesis of V^{4+}–O groups on the support surface (i.e. on silicon) has been performed by the molecular layering - atomic layer deposition (ML–ALD) method introduced in 1970s by St. Petersburg (Leningrad) scientific school [7, 8].

During this synthesis, surface functional groups of silicon reacted with vanadium tetrachloride at 200°C. Reactions 1 and 2 shown below describe single ML–ALD cycle.

$$(\equiv Si\text{-}OCH_3)_m + nVCl_4 \rightarrow (\equiv Si\text{-}O)_m V_n Cl_{n-m} + mCH_3Cl\uparrow, \quad (1)$$

$$(\equiv Si\text{-}O)_m V_n Cl_{n-m} + (n-m)CH_3OH \rightarrow (\equiv Si\text{-}O)_m V_n (OCH_3)_{n-m} + (n-m)HCl\uparrow . \quad (2)$$

Reactions 1 and 2 have been carried out in a gas phase at 200°C in Pyrex reactor in the flow of dry argon. Single crystal silicon (100) plates, pre-treated before the synthesis, have been used as support. The samples were thermally treated under argon atmosphere in Pyrex reactor; treatment duration was 60 minutes. Topography of nanostructures-coated silica has been studied by AFM using microscope Solver P47 Pro in tapping mode in air. 4-5 spots on each sample surface were probed. SEM images of the surface have been recorded on Supra 40 VP microscope using detection method In-Lens SE.

X-Ray photoelectronic spectra have been recorded in vacuum using ESCALAB spectrometer (Dept. of Physics of St. Petersburg State University). Photonic energy calibrated using K_α line of aluminum (1486.6 eV)

X-Ray Diffraction patterns have been measured on diffractometer Thermo ARL X'TRA using thin film collimator at Cu K_α, in the range 2θ = 5 to 60°, sufficient for detection of all relevant reflexes.

3. RESULTS AND DISCUSSION

The support surface ready for synthesis is characterized by high homogeneity degree (Fig. 1). After 1 cycle of ML–ALD, islands of 0.9 nm high and ~ 440 nm linear size (large "islands") are formed in the surface. After 5 ML–ALD cycles "islands" height does not change significantly (1.05 nm), while their width decreased down to 100 nm (Fig. 1). This observation suggests the following scheme of the process (Fig. 2).

First ML–ALD cycle produces "islands" of groups V^{4+}–O on the surface. Within the next cycles, the growth occurs both on already formed particles and on clean surface. Later process occurs with lower intensity that causes stepwise smoothing of roughnesses. This tendency acts until 20th ML–ALD cycle. Sample after 20 ML–ALD cycles has unsignificant roughness of 0.7–0.8 nm, i.e. this is authentic VO_2 nanolayer (Fig. 1). After 40 ML–ALD cycles, the growth mode changes and roughness of the surface is increased – see Fig. 1 for the samples after 40 and 80 ML–ALD cycles. Surface changes are also confirmed by SEM data (Fig. 3).

Powder diffraction data assist in the explanation of the above-described phenomenon. Experimental interplanar spacing data for the samples after 20, 40, and 80 cycles are given in Table 2. Also, for comparison, *d* values from PDF data for VO_2 are presented.

VO_2 layer on silicon surface is shown to be amorphous after 20 ML–ALD cycles (Table 2). Spontaneous crystallization takes place between 20 and 40 cycles. Samples 5 and 6 are of crystalline na-

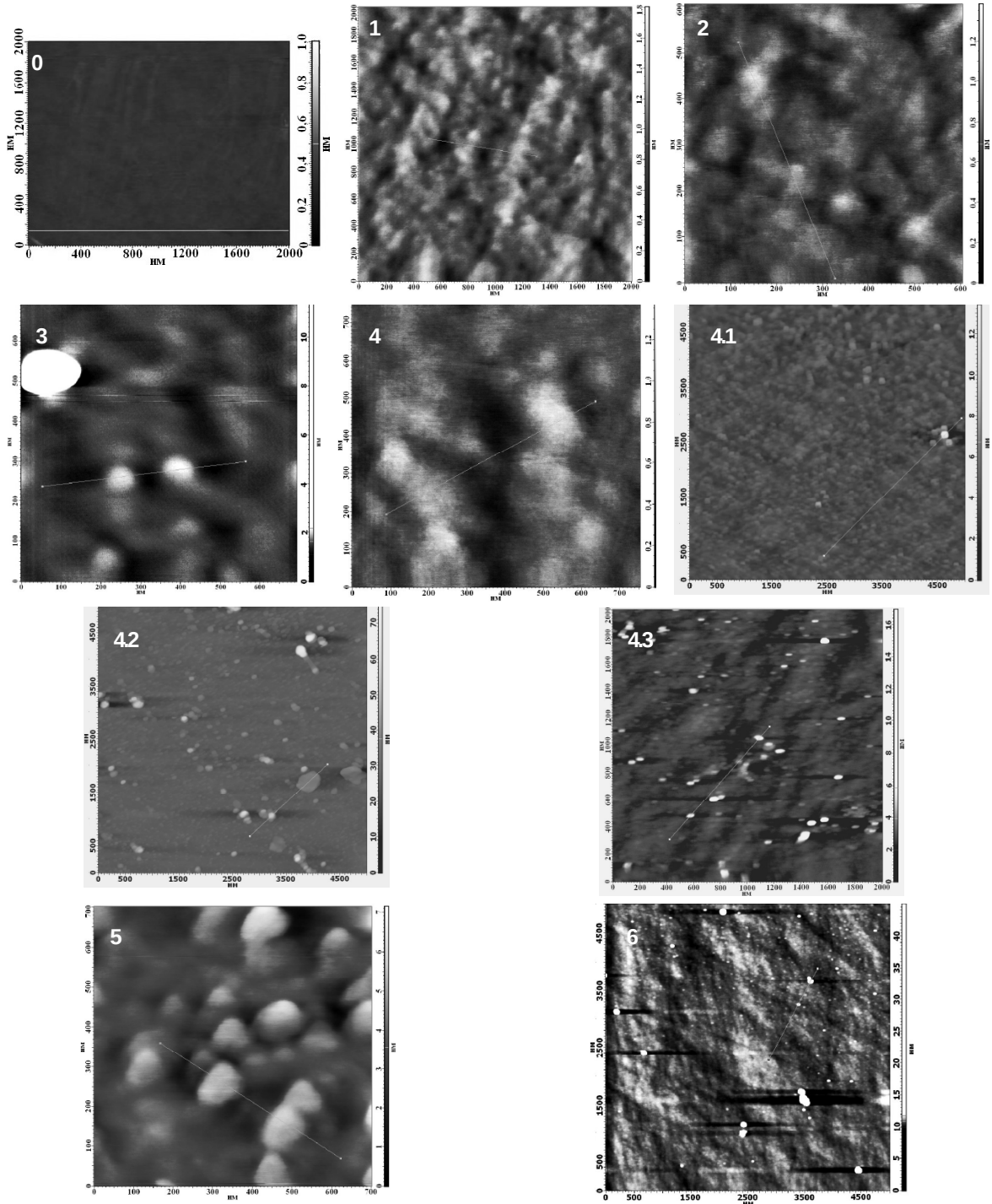

Fig. 1. AFM-images of topography of samples surfaces: *a*) pure silicon (sample 0); *b*) sample 1 after one cycle; *c*) sample 2 after 5 cycles; *d*) sample 3 after 10 cycles; *e*) sample 4.1 after 20 cycles; *f*) sample 5.1 after 40 cycles; *g*) sample 6.1 after 80 cycles.

ture. Sample 5 contains two crystal phases – monoclinic and orthorhombic. Equal peak intensities suggest equivalent amount of these phases in the sample. For sample 6, peak intensity for orthorhombic phase is rather low. Therefore, main phase is monoclinic.

The mixed structure of sample 5 is caused by the spontaneous crystallization. Obviously, amor-

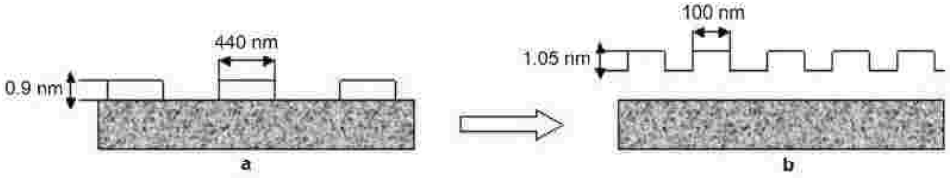

Fig. 2. The scheme of ML–ALD process for VO_2 on silicon surface: (a) 1 ML–ALD cycle, (b) 5 ML–ALD cycles.

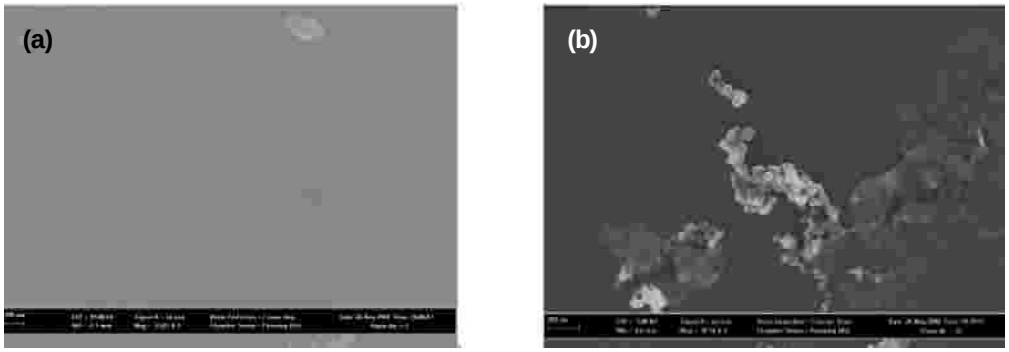

Fig. 3. SEM-microphotographs of samples surfaces: a) after 40 ML–ALD cycles (sample 5); b) after 80 ML–ALD cycles (samples 6).

phous layer is crystallized into more symmetrical orthorhombic structure, whereas the growth on the defects of the as-formed structure leads to monoclinic phase formation. This is also confirmed by the monoclinic structure of the sample 6 that consists of larger crystallites.

The known way of crystallization of amorphous films is the calcination at different temperatures (temperature range depends on the synthesis method as well as on the properties of film component). The sample after 20 ML–ALD cycles (synthesis temperature is 200 °C), that is initially

Table 2. Theoretical and experimental values of interplanar spacings for samples of vanadium dioxide 4, 4.1, 4.2, 4.3, 5, 6.

Sample No.	No. of cycles	D_{exp}	D_{theor}	I, %	PDF card No.	Crystal system, space group	hkl
4	20	No crystalline phase presents					
4.1	20	1.625	1.625		19-1401	triclinic	$02\bar{2}$
							$0\bar{2}2$
4.2	20	1.627	1.62688	5	01-076-0676	orthorhombic F222	333
							800
		1.620	1.6209	100	33-1441	monoclinic C2/m	$\bar{4}02$
4.3	20	1.642	–	85	–	–	–
		1.639	–	100	–	–	–
5	40	1.634	1.6345	100	33-1400	monoclinic P2/m	$\bar{2}02$
		1.632	1.63133	99	01-076-0676	orthorhombic F222	731
6	80	1.628	1.62688	8	01-076-0676	orthorhombic F222	333
							800
		1.622	1.6209	100	33-1441	monoclinic C2/m	$\bar{4}02$

amorhous, crystallizes after thermal treatment. We intended to reveal the temperature of the beginning of crystallization and establish the thermal treatment influence on the surface relief.

The forced crystallization is occurs while heating at 350, 400 or 450 ºC (see Table 2). The higher the treatment temperature, the more symmetrical phase is formed. Due to this observation, we expected the sample 4.3 to be orthorhombic. Surprisingly, interplanar spaces (*d*) for this sample do not correspond to known ones for vanadium dioxide. The best fit of the experimental *d* values suggests an oxygen-deficient oxide V_5O_9. Therefore, in the temperature range of 400–450 ºC synthesized vanadium dioxide VO_2 reduces into V_5O_9.

As already stated above, the sample after 20 ML–ALD cycles without thermal treatment (Fig. 1) is of low roughness. Thermal treatment causes increasing the surface roughness. Cusps are formed, whose height is increased while temperature increasing, while width is decreased. It is explained by crystallites growth from initially amorphous film. The dependence of the relief on the temperature occurs for the samples 4.1 and 4.2. Because of composition changes, there is no such dependence for the sample 4.3.

4. CONCLUSION

It is shown by means of AFM and XRD that morphology and structure of nanosized vanadium dioxide on silica surface depends on the number of ML–ALD cycles.

Based on AFM data, the scheme of vanadium dioxide thin film formation by ML–ALD is proposed.

Based on XRD data, the spontaneous crystallization process is mentioned for amorphous VO_2 film on silica surface. All the crystallites are oriented on the support surface.

It is established that while increasing number of ML–ALD cycles, more symmetrical lattice is formed, therefore, phase composition depends on the number of ML–ALD cycles.

For VO_2 films after 20 cycles of ML–ALD, increasing thermal treatment temperature leads to increasing symmetry of product phase that is accompanied change in the surface relief.

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