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FROM MATERIALS OF ALL-RUSSIAN CONFERENCE "CHEMISTRY OF SURFACE AND NANOTECHNOLOGY"

Synthesis and Electrophysical Characteristics of VO_2-Based Nanostructures with a Complicated Architecture on a Silicon Surface

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Abstract—Nanofilms of complicated architecture based on VO_2 and containing chromium were synthesized by the molecular layering method. The study of electrophysical characteristics of vanadium dioxide nanocrystallites and of VO_2-containing chromium has shown that semiconductor-metal phase transitions appear in the ranges of 130–160 and 100–110 K, respectively. The introduction of a transition-element ion in the nanostructures based on VO_2 affects the phase transition characteristics.

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Owing to the semiconductor-metal phase transition vanadium dioxide films are applied for more than 50 years as a material for devices and instruments realizing a sharp threshold change of electrical, magnetic, and optical properties when certain critical values of exterior parameters (first of all, temperature) are reached [1]. Over the last years a successful development of methods for the synthesis of VO_2 nanofilms has revived the interest of researchers to this subject. The main factors influencing characteristics of the phase transition are the thickness and morphology of films, and also the presence of transition element ions in their composition [2]. Nevertheless the methods of precision regulating of film thickness and of introducing transition element ions are practically not discussed in the literature.

The molecular layering method known also as ALD (Atomic Layer Deposition) is most promising for the synthesis of nanostructures based on vanadium dioxide, as it allows nanosubjects of various composition and structure to be obtained precisely on the surface of monolithic and powder matrices.

In [3] two-dimensional nanostructures of the films based on vanadium dioxide containing chromium and iron were obtained on the surface of a silica model matrix. On the basis of found regularities the necessary synthesis conditions were selected and the mechanism of nanosize VO_2 formation on the single-crystal silicon surface was proposed [4].

In the present work we present the results of the ALD synthesis of VO_2 nanofilms with a complicated architecture, i.e. of structures containing ions of transition elements (in our case, of chromium). The synthesis consists of two stages. The first stage is the surface standardization [reactions (1a), (1b), and (2)], i.e. creating of reactive functional groups of a uniform chemical nature on it.

$$(\equiv Si–OH) + CCl_4 \rightarrow (\equiv Si–Cl) + COCl_2\uparrow + HCl\uparrow, \quad (1a)$$

$$(\equiv Si–O–Si) + CCl_4 \rightarrow 2(\equiv Si–Cl) + COCl_2\uparrow, \quad (1b)$$

$$(\equiv Si–Cl) + CH_3OH \rightarrow (\equiv Si–OCH_3) + HCl\uparrow. \quad (2)$$

The second (main) stage represents reaction (3) of the resulting functional groups with a low-molecular volatile reagent containing an appropriate element in a required oxidation state. Chlorine, which enters into the composition of element-containing functional groups, is further replaced by methoxy groups [reaction (4)] suitable for the ALD process prolongation.

Description of obtained samples

Alternation of oxide layers (specified in relation to the main element)	V–Cr–V	V–Cr–V	V–Cr–V	Cr–V–Cr	Cr–V–Cr
Number of ALD cycles	5–1–5	10–1–10	10–3–10	1–5–1	1–10–1
Molar relation Cr/V	0.14	0.04	0.20	0.30	0.20

Reactions (3) and (4) make one cycle of the molecular layering.

$$(\equiv Si–OCH_3)_m + n ElRCl_k \rightarrow (\equiv Si–O)_m(ElR)_nCl_{kn-m} + mCH_3Cl\uparrow, \quad (3)$$

$$(\equiv Si–O)_m(ElR)_nCl_{kn-m} + (kn-m)CH_3OH \rightarrow (\equiv Si–O)_m(ElR)_n(OCH_3)_{kn-m} + (kn-m)HCl\uparrow, \quad (4)$$

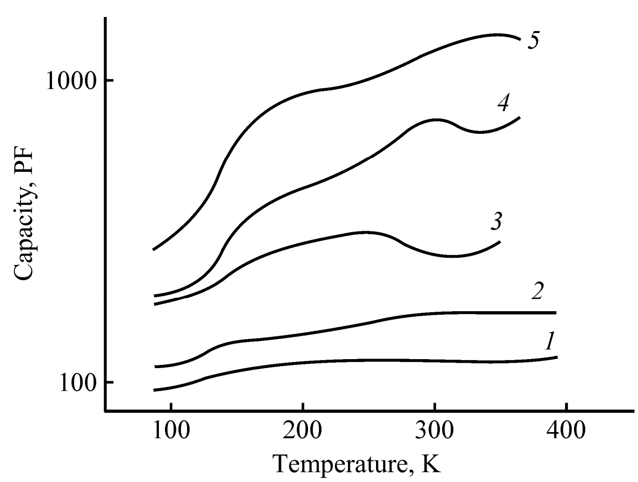
$$ElRCl_k = VCl_4,\ CrO_2Cl_2.$$

Thus, nanostructures with a complicated architecture based on a basic compound and containing a specified amount of an additionally introduced element can be obtained precisely by variation of the number of cycles, the nature of initial low-molecular reagents, and conditions of the synthesis. Characteristics of the synthesized samples are presented in the table. The presence of V^{4+} and Cr^{4+} ions in the resulting structures was confirmed by the magnetochemical analysis [5].

The experiments fulfilled in [4] have shown that up to 40 ALD cycles result in the formation of VO_2 amorphous films, and further the processes of spontaneous crystallization and formation of self-organized nanocrystallites on the silicon surface are observed. It was shown by atomic-force and scanning electron microscopy methods that the formation of amorphous films and then of nanocrystallites is also characteristic for the samples with complicated architecture as the number of ALD cycles increases. A change in the morphology was fixed even after 23 molecular layering cycles (a V–Cr–V sample, the number of cycles 10–3–10), which seems to be caused by the influence of the added element on the nanostructure growth mechanism. The presence and position of the semiconductor-metal phase transition for the obtained samples was determined by measuring temperature dependences of the capacity of the Schottky diode formed on the basis of synthesized nanostructures. Capacities of the nanostructures were measured using various direct voltage shifts from +1 up to –5 V within the temperatures range from 80 up to 400 K.

For the samples obtained as a result of 80 cycles of the VO_2 molecular layering, sharp changes are observed in the capacity vs temperature dependences (see the figure). Two steps are characteristic for these curves: the low-temperature (at 130–160 K) and the high-temperature. Such a character of the dependence is not typical for pure silicon [6]. The high-temperature step is observed at the voltage variation from +1 up to –1 V, and it disappears at further increase in the potential barrier (from –3 up to –5 V), which can be caused by the presence of surface states on the metal-film and film-semiconductor interfaces or on the boundary between nanocrystallites forming the film. The position of the low-temperature step does not depend on the shift voltages, however they affect its value and slightly affect its form. It can be caused by the semiconductor-metal phase transition in the sample, which gives rise to a sharp increase in the built-in charge and (or) in the contacting area.

A similar pattern is also observed for chromium-containing nanocrystallites based on VO_2. The capacity variation is less expressed, which probably is connected with a smaller fraction of vanadium in a sample (2000 and 295 μmol g^{-1}, respectively). The low-temperature step is displaced to the range of 100–110 K, and the high-temperature is recorded at 200 K.



Capacity characteristics of VO_2 nanocrystallites on a silicon surface (80 molecular layering cycles).

EXPERIMENTAL

As a support for the molecular layering synthesis of samples we used single-crystal silicon plate preliminarily polished up to the 14th surface finish classes (surface orientation 100). Primary preparation of the silicon surface consisted in its refining and hydroxylation. Surface standardization and the synthesis of samples were carried out in the gas phase at 350 and 200°C, respectively, in a pyrex reactor in a dried helium flow. Vanadium and chromium amounts were determined by the photometry method according to the standard procedures [7]. The topography of the sample surfaces and of the initial matrix was investigated on a Solver P47 Pro scanning probe microscope by the atomic-force microscopy method in a semi-contact mode in air, and also by the scanning-electron microscopy method (SEM) on a Supra 40VP microscope. The metal-semiconductor contact (the Schottky diode) was produced by aluminum thermal sputtering in the chamber of a VUP-5 vacuum post. The ohmic contact was formed by the InGa-eutectic chafing from the plate back side. Capacity was measured at the 1 MHz frequency at heating from the liquid nitrogen temperature. The SEM and capacity spectroscopy investigations were carried out on the instrumentation of the "Nanotechnology" interdisciplinary resource center of St. Petersburg State University (http://nano.spbu.ru).

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