Technology of vanadium and its oxides based nanocomposite structures

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The peculiarities of vanadium and its oxides based nanocomposite structures fabrication are brought in this paper. The selected fabrication technological conditions allow creating a V_2O_5 based dielectric matrix in which conducting clusters are uniformly distributed. Some optical and electrical properties of such structures are presented. It was shown that the obtained layers possess high charge sensitivity.

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1. Introduction

In the modern microelectronics along with the nanodimensional materials a certain position is taken by the nanocomposite structures the extraordinary electrical properties of which (high charge sensitivity, presence of dimensional effect, functionality) are stimulated by low dimensions of the conducting granules, by the presence of the dielectric interlayer between them and by charge quantification [1-3]. If the energy of charge fluctuations on to conductive granules exceeds the energy of the thermal fluctuations in the medium of the fine granules, there is a phenomenon of Coulomb blockade which is observed in *I-U* dependencies in the form of Coulomb steps, each one corresponding to the charge variation in time on to conductive granules. In this case the conductivity is determined by above-barrier electrons thermal flow [4-5].

In the above mentioned papers the nanocomposite structures were obtained by using thhe scanning tunnel microscope by combining the electron beam lithography and the ion beam deposition.

For practical using the composite layers usualy are fabricated by the sputtering of the combined targets of Al, Ti, Si oxides in which on their entire surface such metals as Au, Pt and other are included. For example in the paper [6] the conductivity, magneto-resistance and Hall effect were studied in the grained nanodimensional Fe/SiO_2 layers, obtained by joint ion-beam sputtering.

In the given paper the results of the investigation of vanadium and its oxides based nanocomposite structures are brought. It is well known that at the temperatures lower than 600 °C, the vanadium oxidation-leads to the formation of the main vanadium oxide V_2O_5, which can be used as a dielectric matrix in the created nanocomposite layers. In the vanadium-oxygen system there are some twenty compounds beginning with the V_2O suboxide and to high V_2O_5 oxide, and besides some of them (V_2O_3 и VO_2) possess the phase transition of the first kind [7]. One can suppose that at the vanadium thin layer oxidation a part of it will go to the formation of V_2O_5 matrix formation, and a part of oxides and the actual vanadium atoms will form the conducting clusters distributed inside of this matrix.

First experiments showed [8] that nanocomposite structures based on vanadium and its oxides can be obtained by the oxidation of vanadium thin layers, both with mirror like as well as fractal surface, on the account of structuring of underlayment (SnO_2-In_2O_3) conductive layer.

One of the main problems of nanotechnology there is a problem of creation of group processing method allowing fabrication of the needed structure onto entire substrate surface or onto its sufficiently large region [10]. In this sense, it is advisable to create the main vanadium layer by the method of vacuum technology allowing to control the given layer thickness on a large amount of substrates, limited only by the vacuum chamber volume.

2. Nanocomposite structures manufacturing

At the heart of creation of the nanocomposite structures based on vanadium and its oxides the principles of self-organization and self-consistency were used. The self-organized structures [11] arise in open type systems exposed to substance inflow from outside, having a certain power to put the system in the region removed from the equilibrium. In such systems, initiated by thermal diffusion, a steady state is set-system properties do not depend on time [11]. If the obtained vanadium layer is heated from the substrate side, then the arising flow of heat is directed to the layer surface and there along. When the layer is exposed to oxygen the concentration flow is directed to the vanadium granules boundary and along the surface. In this case two counter flows affect the vanadium layer-thermal and concentration ones, directed to an angle to one another. By selecting the thickness of vanadium layer, of substrate temperature and of oxygen time exposure the arrangements for the transfer of vanadium-working gas system into a new none-equilibrium state are created. The further thermal annealing of the obtained layers transfer them in the nanostructures based on vanadium and its oxides having steady in time electro-physical parameters.

For fabrication of the vanadium layers a vacuum unit supplied by two electron evaporators with annular cathode, allowing to process up to 40 plates (dimension of each one 48x60mm) and to heat the up to 350^{o}C. The thickness control of the deposited vanadium layers was estimated by the resistance of the witness layer, which was established in the limits of 2-8 kΩ. Before the lapping of oxygen into the vacuum chamber the substrates temperature was increased to 300 ^{0}C. The oxygen exposure time was controlled according to the witness layer resistance increase by two times, after the gas supply and substrates heating up is switched off. The obtained layers were kept into the vacuum chamber approximately 16-20 hours, during this time the witness layer resistance increased by three times relative to the initial one. The witness layer resistance variation in time indicates to the presence of the none-equilibrium states in the obtained structures. The further temperature annealing of the samples in the air at 340-360 ^{0}C during 1hr transfer the entire set of the obtained structures in a new steady state.

The layer structure was studied by using Raman spectra investigation. As one can see in Fig.1 certain peaks the position of which is analogical to those obtained at the investigations of V_2O_5 crystalline layers [12]. The studied layers were subjected to the structuring by using a weak electromagnetic field (50 Hz, peak value 30 mT) during 30 min. As one can see from Fig.1 a slight decrease of the maxima in the Raman spectra without disturbing their position is observed. As a weak electromagnetic radiation can not exert any considerable influence on the vanadium oxide or on the free vanadium atoms, if they do exist there, then one can suppose that in the V_2O_5 matrix volume there are conductive clusters, which contain in their volume the dead bindings [13]. It is on these dead bindings a weak electromagnetic field can affect.

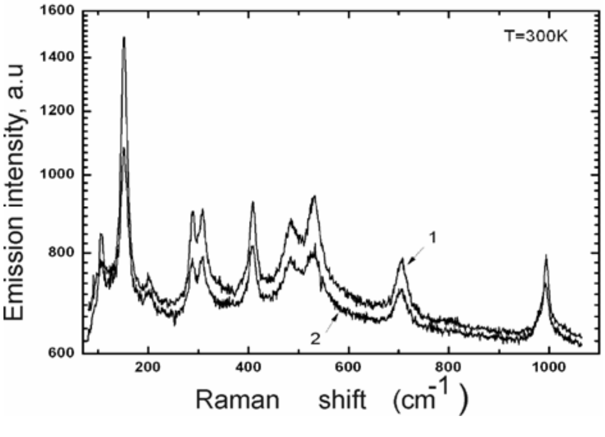
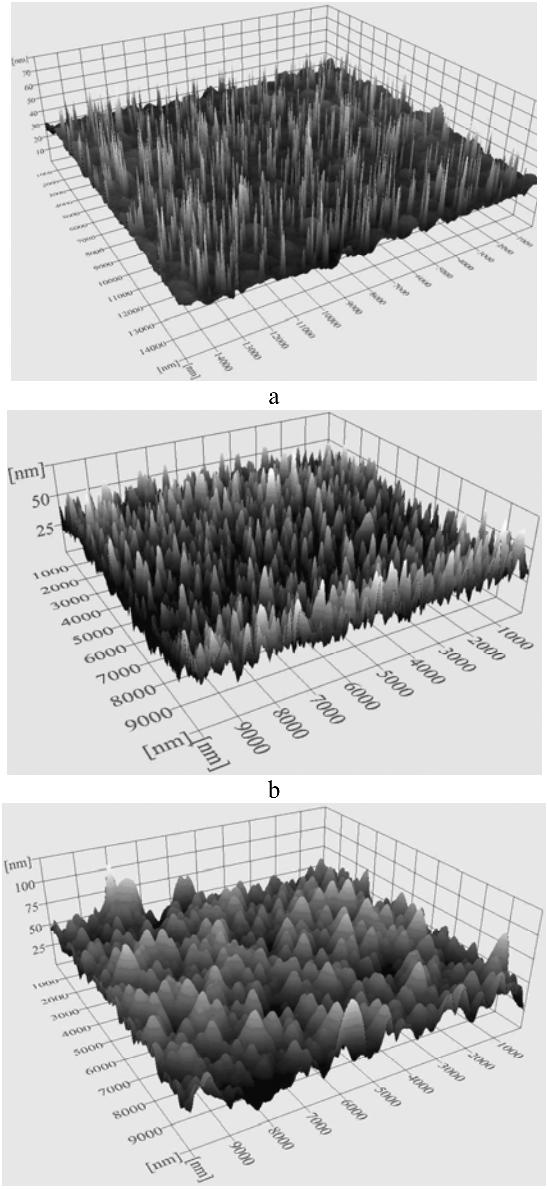


Fig. 1. Raman spectra of the nanocomposite structures: 1-without structuring, 2- after structuring.

The proposed technology allow to obtain stable over time nanocomposite structures based on V_2O_5 vanadium oxide in the volume of which the conducting clusters are distributed.

3. Substrate preparation

For the synthesis of nanocomposite structures the surfaces maximum free of the impurities, structural imperfections and irregularities are needed. The most suitable substrates for nanocomposite layers fabrication, in our opinion, the usual pyroceramics, possessing the mirror like surface can be used. As the (AFM studies SIS-scan control) had shown (Fig. 2.1) the degree of heterogeneity of the pyroceramics surface is rather high and is of the order of magnitude of the nanocomposite structures thickness.



a

b

c

Fig. 2. Three dimensional AFM images of the surfaces of pyroceramics (2.1), nanocomposite structures obtained by using the transition vanadium-aluminum layers (2.2) and of nanocomposite structures obtained by using the PC3710 vanadium-aluminum resistive alloy (2.3).

For pyroceramics surface irregularities decrease, from the practical point of view, the simplest solution is creation of the thin transition layer and the growth on its surface of the nanocomposite structure. Such transition layer on pyroceramics can be made by the aluminum metallization with the chromium or vanadium sub-layer acting as an adhesive. The grown on such surface nanocomposite layers possessed certain homogeneity, but continued to maintain the structure of the surface of the glass-ceramic. By estimating the nanocomposite composition by electron microscope (Fig. 3.1) we did not observe the vanadium own reflections that have been "smeared" by glass-ceramic elements.

If between glass ceramic and the vanadium sub-layer to introduce an additional layer of PC3710 resistive alloy then the electron microscope studies reveal the diffraction maxima corresponding to vanadium (Fig.3.2). That is, the thickness of the intermediate layer should be considerable.

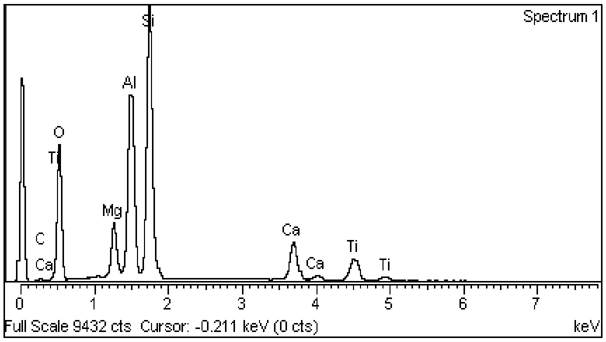


Fig. 3.1. The nanocomposite structures composition obtained by using the vanadium-aluminum transition layer.

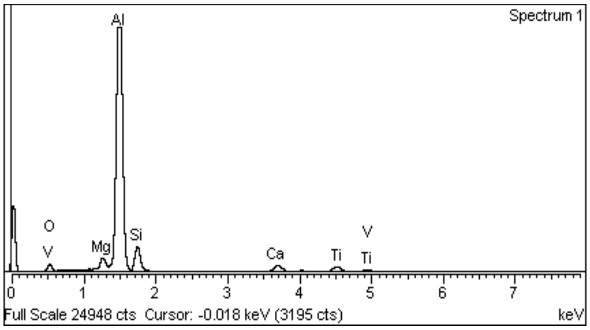


Fig. 3.2. The nanocomposite structures composition obtained by using the PC3710 resistive alloy transition layer.

Three dimensional AFM images of the surfaces of pyroceramics (Fig. 2.1), nanocomposite structures obtained by using the transition vanadium-aluminum layers (Fig. 2.2) and of nanocomposite structures obtained by using the PC3710 vanadium-aluminum resistive alloy (Fig.2.3). It can be seen that with increasing thickness of the transition layer reduces the surface roughness.

The nanocomposite structures obtained on pure silica substrates are the replica of the substrates.

The nanocomposite structures obtained in the indicated thickness range of the initial deposited vanadium layer, had the thickness does not exceeding 30-40 μm.

4. Optical properties

The investigation of the optical properties of the nanocomposite structures were carried out on the nanocomposite layers formed on silica substrates in the same single cycle with the layers on the metalized sitall substrates. The studies of the reflection and transmission spectra were carried out on a Jasco640 two-beam spectrometer at a room temperature. As one can see from Fig. 4 in the reflection spectra two peaks at 2,89eV and 4,34eVare observed which could not be related to the interference, due to the fact that they are present in the all spectra of the measured samples series, and their position is consistent. The law value of the nanocomposite structures thickness does not allow high quality measurements of the reflection spectra. In the transmission spectra of the studied nanocomposite structures the absorption edge is clearly expressed, which allow to estimate their band gap as 3,09 eV. The peculiarities observed in the reflection and transmission spectra according to [14] could be related to the electron transitions from different valence bands in the conduction band.

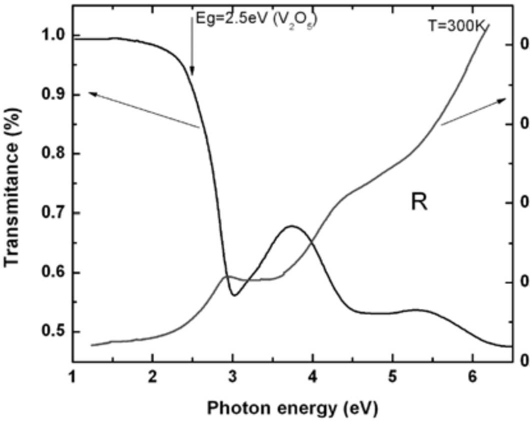


Fig. 4. Nanocomposite structures reflection and transmission spectra.

Structuring of the nanocomposite layers by a weak electromagnetic field (50 Hz, 30 mT, 30 min) slightly increases the peaks height in the absorption spectra without changing their position.

The constancy of the reflection and transmission spectra measured n the different sample points, indicates to a good optical quality of the layers and witnesses about high homogeneity of the nanocomposite structures obtained on considerable areas of the silica substrates.

5. Electrical properties

In the transversal direction the layer resistance does not exceed 1,5-3,0 Ohm and the temperature resistance coefficient (TRC) is always positive , which corresponds to the metallic type of conductivity. At the measurements if the I-U temperature dependence in the transversal direction, it was established that at the temperature of 144^0C and the voltage of 270 mV the abrupt layer transition from conductive to dielectric state is observed and the current through the sample decreases to zero (Fig.5). If you remove the power supply and remove the remaining charges from the sample surface by connecting to the ground then again the I-U measurements are the same as initial with the phase transition at U_{inv}.=270mV (Fig. 5).

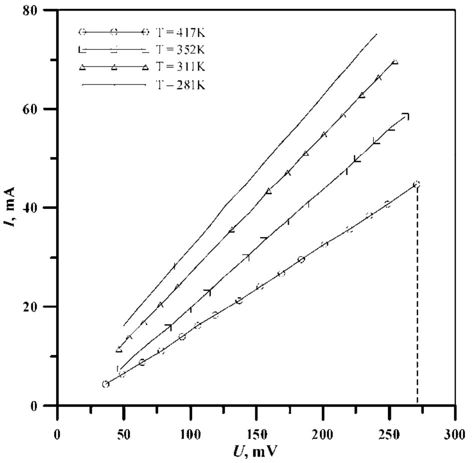


Fig. 5. Nanocomposite structure I-U dependencies at different temperatures.

The second type phase transition is observed only in the case when the diameter of the upper electrode does not exceed 7-10 μm that is revealed the pronounced dimensional effect.

By varying the layer thickness and the conductive cluster dimension one can control the temperature of the phase transition in the limits of 110-150^0C.

It should be noted, that the presence of the dimensional effect in the obtained nanocomposites witnesses about uniform distribution of the conductive clusters in the entire volume.

At the investigation of I-U dependencies of the nanocomposite structures at room temperature one can see that at the change of the charge state of the conductive clusters occurs with the voltage increase, which organize “bigger” clusters, which lead to the structure internal resistance decrease and stipulates the current increase through the sample on anew higher level by preserving the I-U dependence linearity (Fig.6.1). When the input voltage is higher than the steady second level, then the transition to higher level occurs. At the voltage decrease the I-U linearity remains at the given level up to a certain voltage, after which a transition to lower level occurs by hopping. In dependence on the applied voltage the transition from the first level to a third one (or even higher), but the charge state levels itself of all samples obtained in a single technological cycle are the same. The transitions by hopping could be explained by the formation (or destruction) of bigger (or smaller) clusters on the account of Coulomb electrons.

If the nanocomposite layer is structured by a weak electromagnetic field (50 Hz, peak value 30 mT) then a structure is revealed, when from the lower level to the closet higher one transitions are observed, without changes in the energetic state of the system (Fig.6.2).

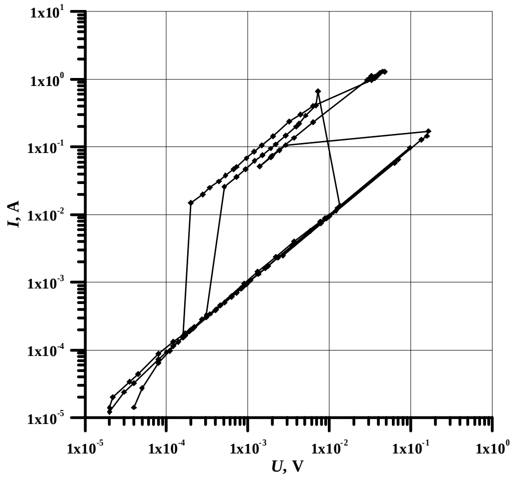


Fig. 6.1. I-U dependencies at room temperature of nanocomposite structure before structuring.

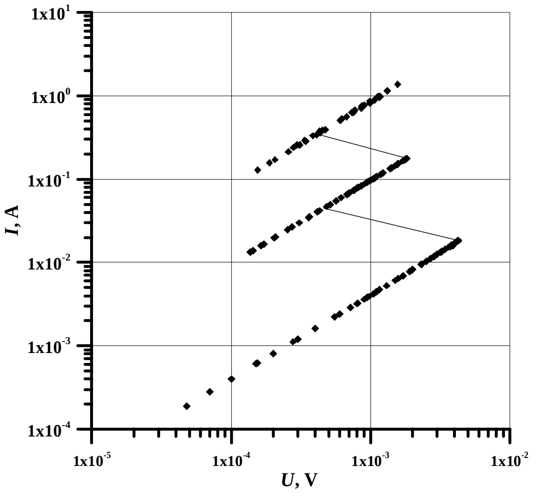


Fig. 6.1. I-U dependencies at room temperature of nanocomposite structure after structuring.

6. Conclusions

The proposed technology of nanocomposites fabrication allows to create the V_2O_5 based structure in the entire volume of which the conductive clusters are distributed.

The obtained nanocomposites in group performance possess a high optical homogeneity on a rather large area.

The vanadium based nanocomposites possess high charge sensitivity.

The possibility of vanadium based nanocomposite structure properties control by weak electromagnetic field was shown

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References

[1] P. Sheng, B. Abeles, M.D. Coutts, Y. Aril, Adw. in Phys. **24,** 408 (1975).

[2] Andersen F. Lokalinye momenty i lokalinye sostoiania. UFN., **1**(76), 19 (1979).

[3] U. V. Medvedev, A. M. Grishin, FTP, **1**(5), 900 (2001).

[4] C. Schonenberger, H. Van Houten, H. C. Donkerstoot, Europhys. Lett., **20**, 249 (1992).

[5] W. Chen, H. Ahmed, K. Nakazoto, Appl. Phys. Lett. **66**, 3383 (1995).

[6] B. A. Arozon, A. E. Varfolomeev, D. I. Kovalev, FTT, **41**(6), 944 (1999).

[7] D. A. Davydov, A. I. Gusev, FTT, **51(**1), 147 (2009).

[8] V. D. Prilepov, P. A. Gasin, A. B. Chirita, D. A. Spoiala, Technical Physics, **55**(5), 747 (2010).

[9] I. N. Serov, B. A. Jabreev, V. I. Margolin, Fizica i Himia stekla, **29**(2), 242 (2003).

[10] G. Nikolos, N. Prigojin, Samoorganizatsia v neravnovesnyh sistemah. M:"Mir", 1979, p.512

[11] B. C. Bokshtein, Diffuzia v metallah. M. Metallurgia 1978.

[12] Se-Hee Leea, at al. Solid State Ionics, **165,** 111 (2003).

[13] B. I. Shklovskii, A. L. Efros, Elektricheskie svoistva legirovannyh poluprovodnikov.. M:"Mir", 1979 p.166-484.

[14] Szaboles Beke, Thin Solid Films, **519**, 1761 (2011).

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