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BRIEF COMMUNICATION

Neodymium–Vanadium Oxide Bronze Thin Films[1]

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The possibility of preparing neodymium–vanadium oxide bronze thin films by magnetron sputtering of either a mixture of $NdCl_3$ and V_2O_5 or a mixture of Nd_2O_5 and vanadium oxides in an argon atmosphere is examined. The chemical composition and X-ray structural analysis of the prepared samples are presented. It is found that the films crystallize into the monoclinic crystallographic system and their composition is in line with the formula $Nd_x^{3+}V_{2-3x}^{5+}V_{3x}^{4+}O_5^{2-}$. © 1994 Academic Press, Inc.

The vanadium oxide bronzes are promising materials for the development of the diverse ionometrical sensors, including microelectronic ones (1). In this connection there is an urgent need to explore the perspectives as well as to find efficient methods of producing thin films of these materials.

By now there has been an attempt at making lithium–vanadium bronze thin films by reactive magnetron sputtering of metallic vanadium in an argon atmosphere doped with a small amount of oxygen followed by electrochemical treatment in $LiClO_4$ (2). However, the sputtering of the bronze itself or of a stoichiometric mixture of its ingredients appears to be more promising because the amount of cation that is introduced into the V_2O_5 lattice can be regulated more accurately. The second method of film preparation is especially tempting because it does not demand the initial material synthesis, which frequently is a complicated and labor-consuming technological process. For example, the synthesis at rather high temperature of lanthanide–vanadium oxide bronzes turns out to be successful only under high (7.7–9.0) GPa pressures (3). It is quite probable that it is these conditions of synthesis that are responsible for the distinctive features of the crystal structure of the materials: the β-phase of these bronzes crystallizes into hexagonal crystallographic system instead of into the usual monoclinic one (1, 3).

We examined the possibility of the growth of oxide bronzes by the method of stoichiometric mixture sputtering, in particular the preparation of neodymium–vanadium bronze thin films. The results of these investigations are reported in the present paper.

The disk-shaped targets of 25 mm diameter and 2 mm thickness used in the sputtering were formed under 8×10^8 Pa pressure from powders of $NdCl_3$, Nd_2O_3, and vanadium oxide mixtures in accordance with the reactions

$$x\mathrm{NdCl_3} + \mathrm{V_2O_5} = \mathrm{Nd}_x\mathrm{V_2O_5} + \tfrac{3}{2}x\mathrm{Cl_2}, \quad [1]$$

$$x\mathrm{Nd_2O_3} + (2 - 3x)\mathrm{V_2O_5} + 3x\mathrm{V_2O_4} = 2\mathrm{Nd}_x\mathrm{V_2O_5}, \quad [2]$$

$$x\mathrm{Nd_2O_3} + (2 - \tfrac{3}{2}x)\mathrm{V_2O_5} + \tfrac{3}{2}x\mathrm{V_2O_3} = 2\mathrm{Nd}_x\mathrm{V_2O_5}. \quad [3]$$

Polyvinyl alcohol of the amount of 1% of the total powder weight has been used as a means for binding the ingredients. The mixtures and the pressed targets were heated in an argon atmosphere at 820 K for 1 hr.

The magnetron sputtering was performed on the unheated glass substrates in a regime of direct current in an argon atmosphere at a gas pressure of (5.0–6.5) Pa. The glow discharge current was (35–40) mA and the sputtering rate was (1.4–1.7) Å/sec. The film thickness was (0.2–2.0) μm.

The films produced in this way turned out to be amorphous. Their crystallization was carried out in air at (670–770) K for 1 hr.

X-ray structural analysis of targets and prepared samples was done. In addition, a chemical composition analysis of film surface using X-ray photoelectron spectroscopy (XPS) was also done. The X-ray diffraction patterns were recorded using the diffractometer DRON-2 (made in the U.S.S.R.) with a Cu$K\alpha$ radiation source and the XPS spectra using the spectrometer XSAM-800 of the Kratos analytical firm.

After the above-described thermal treatment of the targets, their roentgenograms practically preserved their previous character; i.e., they mainly represented the sums

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TABLE 1
X-Ray Data on $Nd_{0.17}V_2O_5$ Thin Film

hkl	d (Å) Calculated	d (Å) Observed	I/I_0 (%)
002	7.22	7.21	26
102	4.82	4.82	33
20$\bar{2}$	4.42	4.45	11
200	4.34	4.34	20
201	3.82	3.83	13
004	3.61	3.63	100
20$\bar{4}$	3.38	3.37	20
30$\bar{2}$ 10$\bar{5}$	3.06	3.06	20
112	2.931	2.932	16
20$\bar{5}$	2.888	2.888	12
21$\bar{3}$	2.694	2.710	59
014	2.582	2.578	17
21$\bar{5}$ 015	2.275	2.272	12
30$\bar{6}$ 40$\bar{1}$	2.255 2.257	2.256	10
400	2.169	2.167	17
41$\bar{1}$	1.926	1.928	10
11$\bar{7}$ 313	1.876 1.877	1.875	28
215	1.828	1.829	9
120	1.805	1.804	9

Note. The magnetron sputtering target was made from a mixture of $NdCl_3$ and V_2O_5. d is interplanar distance; I/I_0 is relative intensity of X-ray diffraction peak.

of the roentgenograms of the chemical compounds of which the powders used for the production of the targets consisted. X-ray diffractograms of the crystalline films made under the same conditions were qualitatively similar to the targets of all types. In addition, the films, in contrast to the bronzes synthetized in (3), crystallized into a monoclinic crystallographic system similar to the β-phase of vanadium oxide bronzes (1). The typical experimental and calculated values of the interplanar distances for the films produced using a target made from a V_2O_5 and $NdCl_3$ mixture are presented in Table 1. The mean unit cell dimensions determined using the basic X-ray diffraction peaks for the investigated films are $a = (9.336 \pm 0.140)$ Å, $b = (3.662 \pm 0.029)$ Å, $c = (15.478 \pm 0.159)$ Å and $\beta = (110.15 \pm 0.75)°$. They are close to the corresponding parameters of the β-phase of vanadium oxide bronzes with alkaline and alkaline-earth elements introduced (1) as well as to those for lanthanum–vanadium bronze (4).

In the composition of the films both V^{5+} and V^{4+} components were revealed.[2] In addition, the ratio of total vanadium concentration to that of neodymium and oxygen is in good agreement with that calculated by the formula for vanadium bronzes of the general form $M_x^{n+}V_{2-nx}^{5+}V_{nx}^{4+}O_5^{2-}$ (1) (see Table 2). In addition, the electric conductivity of the crystalline films is found to be by several orders larger than the conductivity of the targets before thermal treatment.

The above-mentioned results show that the studied films, in the main, have the features of oxide bronzes (1). Hence we can draw the conclusion that the magnetron sputtering of the stoichiometric mixture of the chemical compounds, in accordance with the left side of Eqs. [1]–[3], in the inert gas atmosphere is an acceptable method for forming neodymium–vanadium bronze thin films.

As regards the electrode properties of our films, they essentially depend on sample technology. The films had the greatest sensitivity, for instance, to the hydrogen ion

[2] The V $2p_{5/2}$ core level XPS spectrum exhibits two distinct peaks at binding energies 517.2 and 516.4 eV. The peak at higher binding energy is assigned to the vanadium ion V^{5+} and the second to V^{4+}. This is also confirmed by our earlier XPS measurements of the V $2p$ line in VO_2 and V_2O_5.

TABLE 2
Chemical Composition of $Nd_xV_2O_5$ Thin Films According to Data from X-Ray Photoelectron Spectroscopy

Ion	Film A (the target is from $NdCl_3$ and V_2O_5 mixture) Observed	Film A Calculated ($x = 0.16$)	Film B (the target is from Nd_2O_3, V_2O_5 and V_2O_4 mixture) Observed	Film B Calculated ($x = 0.22$)	Film C (the target is from Nd_2O_3, V_2O_5, and V_2O_3 mixture) Observed	Film C Calculated ($x = 0.15$)
Nd^{3+} (%)	2.4 ± 0.2	2.2	3.3 ± 0.3	3.0	2.3 ± 0.2	2.1
V^{4+} (%)	6.0 ± 0.8	6.6	8.4 ± 0.9	9.0	5.7 ± 0.7	6.3
V^{5+} (%)	22.6 ± 0.9	21.3	19.3 ± 0.9	18.7	22.0 ± 0.9	21.7
O^{2-} (%)	69 ± 2	69.8	69 ± 2	69.3	70 ± 2	69.9
$V^{4+} + V^{5+}$ (%)	29 ± 2	27.9	28 ± 2	27.7	28 ± 2	28.0

Note. Calculations were performed using the formula $Nd_x^{3+}V_{2-3x}^{5+}V_{3x}^{4+}O_5^{2-}$ (1).

in the solution when they were prepared by sputtering the mixture of $NdCl_3$ and V_2O_5. In this case the angle coefficient of E(pH) dependence, where E is electromotive force between the reference and bronze measuring electrodes of the voltaic cell, was (59.3 ± 0.9) mV/pH. In addition, the linear dependence of E(pH) on hydrogen ion activity was found in a large (from 1 to 12) pH range. In conclusion, these films can be of interest for pH ionometry.

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