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Structural and Electro-physical Properties of Heterogenous Film Materials Based on Refractory Metals

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In this paper an electro-physical properties and structural phase composition analysis of heterogenous film materials based on refractory metals is presented. A thermal activity nature of their conductivity was determined. As a result of investigation were estimated thermal resistance coefficient and electro-conductivity activation energy.

Keywords: Heterogenous films, Temperature resistance coefficient, Electro-conductivity, Activation energy.

1. INTRODUCTION

At the modern stage of microelectronics, sensors technology and materials science development an investigation of micro-structural and electro-physical properties of heterogenous film materials based on refractory materials which consist amorphous phase, oxidations, carbides, nitrides, etc, take a higher attention. In resent works [1-7] were discussed a formation features of structure-phase composition and electrophysical properties of analogue patterns.Was made a conclusion about the possibility of their usage as thermal stable sensitive elements of thermal and strain gauge transducers.

At the thermal treatment of heterogenous films in the range of intermediate temperatures are fixed different conductivity types which should be explained as a primary influence of varying component. Taking into account this fact, an object of this article is study of electro-physical properties of heterogenous reference metal films, in particular – to obtain information about their resistivity, temperature resistance coefficients (TRC) and activation energies of electro-conductivity based on the temperatures dependencies of the resistivity.

2. EXPERIMENTAL DETAILES

To obtain films was used vacuum equipment VUP-5M (gas pressure in vacuum chamber was $\sim 10^{-3}$-10^{-4} Pa). Heterogenous structures were formatted by electron-beam evaporation technique at varied an average condensation velocity ($\dot{\omega}$), substrate temperature (T_s) and annealing temperature (T_a). For temperature dependencies obtaining were carried out thermal stabilization cycles "heating – cooling" three times in the temperature range $T = (300\text{-}750)$ K. TRC value and activation energies were determined as a slope angle tangent of temperature dependencies (by relative resistance and natural logarithm changing accordingly).

A devices for films obtaining and their further investigation were placed inside the vacuum chamber. Were controlled electric resistance (accuracy was ± 0.05 %) and substrate temperature (accuracy was ± 10 %).

Phase composition analysis and structural investigation of obtained films were carried out by electron-graph and transmission-electron microscopy (TEM) methods using SELMI PEM-125K electron microscope.

Infrared (IR) spectra of as-deposited and annealed at 750 K heterogenous films on glass-ceramic substrates were estimated by Fourier-transform infrared (FTIR) Agilent Cary 630 spectrometer. FTIR spectra were obtained in full-refraction regime (Diamand ATR appliance). Frequencies absorbance range was varied from 4000 till 400 cm^{-1}.

3. RESULTS AND DISCUSSION

It is necessary to describe more detailed an obtaining conditions and phase composition of refractory metal heterogenous films (TEM-methods).

Condensed Mo films had an amorphous structure at the next conditions: substrate temperature was $T_s = 300\text{-}370$ K and condensation velocity was $- \dot{\omega} < 0.2$ nm/s. By increasing of the substrate temperature to 500 K and condensation velocity – to 0.8 nm/s were formed fine-dispersed crystalline structure with next phase types: face-centered cubic lattice (fcc) – $Mo(C, N)_x$ and body-centered cubic lattice (bcc) – Mo (lattice parameters were – 0.419 and 0.314 nm correspondingly). After films thermal annealing during 15 minutes at 750 K and their further cooling (to room temperature) phase composition was: bcc-Mo + hex-$Mo_2(C, N)$ [1, 2]. At similar conditions is also present an oxide phase cubic-Mo_3O (lattice parameter – 0.499 nm) [3]. So, in Mo heterogenous films present a possibility of oxidations, carbides and nitrides impurities formation.

At condensation velocity $\dot{\omega} = 1.0$ nm/s and substrate temperature $T_s = 400$ K were formed heterogenous films face-centered close-packed lattice (fccp)-Re + fcc-$Re(N, O)_x$. Lattice parameters for meta-stable fcc-phase of rhenium oxidation nitride were: by as-deposited films – 0.405 nm, annealed films – 0.404 nm [1]. On TEM-graphs of heterogenous Re + $Re(N, O)_x$ films a different contrast was fixed. It may be caused by formation of the dark crystallites with nitrogen excesses and bright crystallites – oxygen excesses. Decreasing of the condensation velocity (to 0.1 nm/s) and substrate temperature (to 300-350 K) reduces, similar to the previous investigation, to amorphous phase films formation. By changing of the electron beam intensity were observed point reflexes from hexagonal Re_3O and cubic ReO_3 phases as a result of the amorphous state crystallization [1].

Results of investigations of tungsten (W) base films shown that at $\dot\omega = 0.1$ nm/s and $T_s = 400$ K were formed amorphous films. After their thermal annealing till 750 K was observed a-W+W$_3$O heterogenous composition. It confirms by the formation of another contrast compare to amorphous matrix which corresponds to W$_3$O base-cubic oxide. Further increase of the substrate temperature and condensation velocity follows to formation of nanosize-dispersed W films which have bcc-structure looks like to the massive patterns. After thermal annealing of bcc-W + fcc-W(C, O)$_x$ till 750 K on electron-graph was fixed a weak-smoothed ring which corresponds to carbon-oxide W$_2$(C, O) (fig. 1a).

Vanadium (V) films phase composition is estimated by condensation conditions and their further annealing. While condensation velocity was lower than 0.3 nm/s and substrate temperature $T_s < 320$ K, V films have an amorphous structure. When $\dot\omega$ was 1.2-1.3 nm/s observed formation of bcc-V crystalline phase (lattice parameter was 0.302 nm [8]). After thermal annealing of as-deposited V films in vacuum till 800 K was fixed an increasing of the lattice parameter to 0.416 nm. It may be caused by dilution of the impurity atoms and fcc-VO$_x$ formation [4]. Analogue to the last cases it should be noted that formation of heterogenous bcc-V + fcc-V(C, O)$_x$ films fixed at deposition onto heated substrate (temperature $T_s = 380$-420 K). After their annealing at 750 K in vacuum chamber we observed on electron-graphs a diffraction rings, which may be identify as a V$_2$(C, O) carbon-oxide (fig. 1b).

TEM-analysis results are not able to identify the impurity phases presented in heterogenous films. So, this effect may be proofed by FTIR spectroscopy technique.

It is well-known [9] that most of carbonyl complexes have strong and distinctive valence-band mods ν(CO) at ~ 2100-1800 cm^{-1} since cyanide-complexes ν(CN) lay in the range of ~ 2200-2000 cm^{-1}; CN and CO free-band groups have a frequencies 2080 cm^{-1} and 2155 cm^{-1}; by metal-(CN) group connection ν(CN) line shifted to higher frequencies since CO complexes have an inversed character.

In all investigated films there is no absorption in the spectral region 2500-3500 cm^{-1}, which confirms the purity of the condensates without any moisture and contamination from vacuum pump oil [10].

On fig. 2 mode line at 2310-2330 cm^{-1} corresponds to NO$^+$ (nitrosyl-ion); peak at 2000-2100 cm^{-1} corresponds to CO in carbonyl metals M(CO)$_x$ (M is Mo, Re or V) and at 2090-2100 cm^{-1} - to CN in M(CN)$_x$; mode line on 1110-1090 cm^{-1} connects to NO$^-$ or stretching vibrational mode M=O (M is Mo [9] or V [10]). At the same time mode line at 973 and 491 cm^{-1} (fig. 2a) also corresponds to Mo=O connection in MoO$_x$ [11]. Mode lines at 877, 846 and 631 cm^{-1} (fig. 2b) correspond to ReO$_x$ compound. Mode peaks at 840 and 637 cm^{-1} (fig. 2c) correspond to VO$_2$ compound [12]. Mode line at 440-450 cm^{-1} may corresponds to M-CO or M-C connections. FTIR spectra shown on fig. 2 have a similar view. It may be caused by the same deposition conditions and patterns treatment.
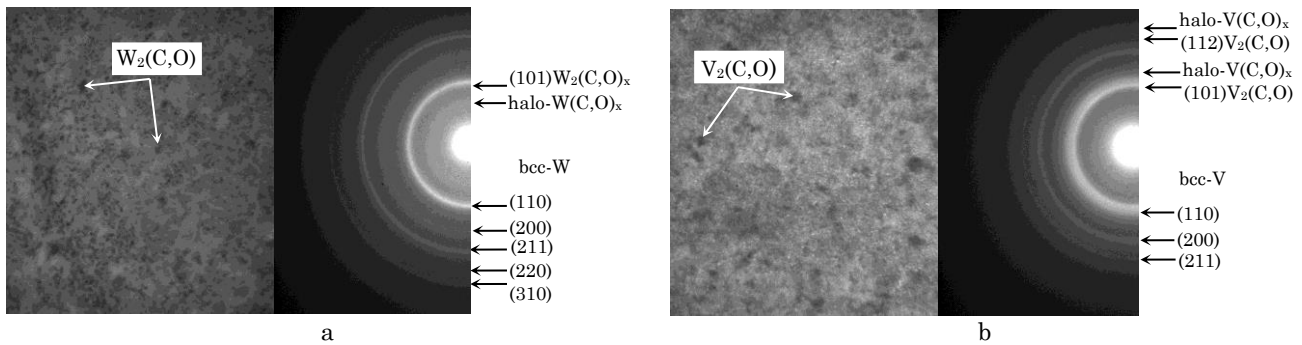

Fig. 1 – Crystalline structure and diffraction pattern of bcc-W + W(C, O)$_x$ (a) and bcc-V + V(C, O)$_x$ (b) annealed at 750 K films

Table 1 – The interpretation of diffraction pattern for annealed heterogenous films bcc-W + W(C, O)$_x$ (a) and bcc-V + V(C, O)$_x$

| №		bcc-W + W(C, O)$_x$				№		bcc-V + V(C, O)$_x$			
	I, a.u.	d_{hkl}, nm	hkl	phase	a, nm		I, a.u.	d_{hkl}, nm	hkl	phase	a, nm
1	halo	0.327	-	W(C,O)$_x$	-	**1**	V H	0.224	101	V$_2$(C,O)	-
2a	V H	0.227	101	W$_2$(C,O)	-	**2**	l	0.214	110	bcc-V	0.302
2b	V H	0.224	110	bcc-W	0.316	**3**	halo	0.204	-	V(CO)$_x$	-
3	m	0.158	200	bcc-W	0.316	**4**	m	0.151	200	bcc-V	0.302
4	l	0.129	211	bcc-W	0.316	**5**	m	0.123	211	bcc-V	0.302
5	V m	0.112	220	bcc-W	0.316	**5a**	m	0.123	112	V$_2$(C,O)	-
6	m	0.100	310	bcc-W	0.316	**6**	halo	0.119	-	V(CO)$_x$	-
	$\bar{a}$(bcc-W) = 0.316 nm; a_0(bcc-W) = 0.316 nm [8]						$\bar{a}$(bcc-V) = 0.302 nm; a_0(bcc-V) = 0.302 nm [8]				

VH – very high, m – medium, l – low.
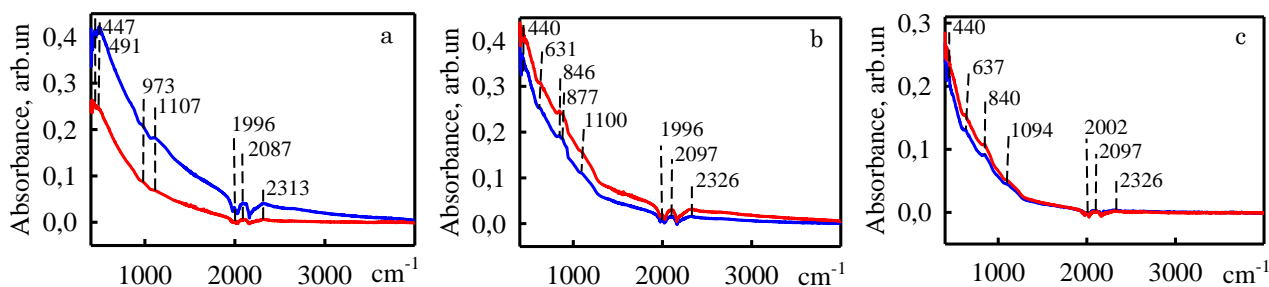
Fig. 2 – FTIR spectra for Mo + Mo(C, N)$_x$ (a), Re + Re(N, O)$_x$ (b) and V + V(C, O)$_x$ (c) thin films (blue - as-deposited; red- annealed at 750 K films)
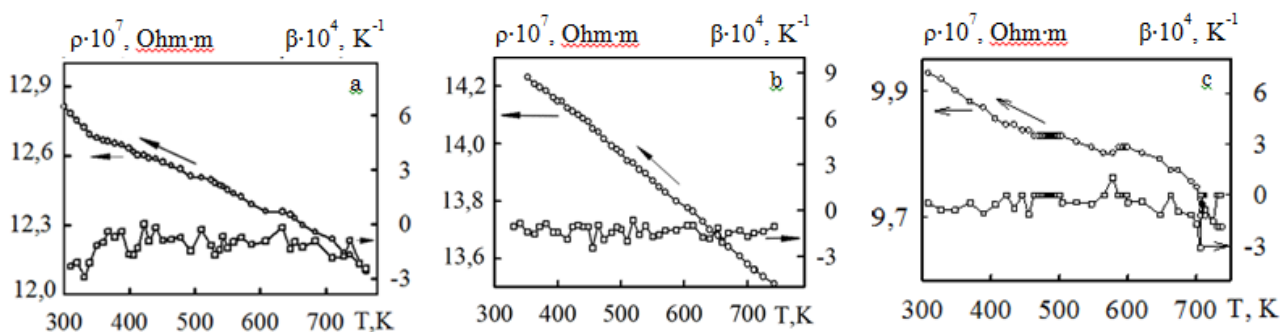

Fig. 3 – Dependences resistivity (TRC) vs. temperature for thin film Mo + Mo(C, N)$_x$, Re + Re(N, O)$_x$ and V + V(C, O)$_x$. Films thickness was 40 nm

In all cases by temperature increasing films reflectivity was decreased. As a result TRC values had a negative view $(10^{-4}$ К$^{-1})$. These results make a possibility to estimate a numerical analysis of electro-conductivity heterogenous films activation energy. Its average value is correspondingly $\sim 10^{-2}$ eV. In V + V(C, O)$_x$ films at $T_s = 440$-520 К was fixed a stability of resistivity and TRC values. It may be caused by activation processes (II phase transition). This effect is typical to V$_2$O$_3$ oxide phase. It should be noted that critical temperature value is well-correlated with [4].

Electro-conductivity activation energy measurement of refractory metals heterogenous films shown that it is closed to the thermal fluctuation energy. Such low values of energy correspond to the practical absence of the impurity phases in investigated films with semiconductor properties.

4. CONCLUSIONS

As a result of investigation in the range of intermediate temperatures for V + V(C, O)$_x$, Mo + Mo(C, N)$_x$ (W + W(C, O)$_x$) and Re + Re(N, O)$_x$ heterogenous films was fixed a thermal active nature of the conductivity – at decreasing of temperature resistivity increases. Electro-conductivity activation energy has a value much lesser (10 times) compare to the thermal fluctuation energy. TRC was practically not changed and had only negative values $\sim 10^{-4}$ К$^{-1}$. Obtained results may be caused by the presence in heterogenous films a lot of intermetallic phase which increases at increasing of the films thickness. FTIR spectra of investigated films shown that they have mode lines preferentially correspond to CO, CN and NO-complexes which characterized about the heterogenous nature of condensates.

REFERENCES

1. I.P. Buryk, L.V. Odnodvorets, *J. Nano- Electron. Phys.* **1** No 3, 24 (2009).
2. L.V. Odnodvorets, N.I. Shumakova, O.P. Tkach, I.Y. Protsenko, *J. Nano- Electron. Phys.* **1** No 1, 29 (2009).
3. S.V. Petrenko, I.E. Protsenko, M.D. Smolin, *Izv. Vuz. Phiz+* **2**, 90 (1986).
4. T.M. Grychanovs'ka, I.Yu. Protsenko, A.M. Shkira, *Visnyk SumDU. Seriya Fizyka, Matematyka, Mekhanika* **13** No 46, 101 (2002).
5. S.P. Novosyadlyi, V.M. Vivcharuk, V.P. Peregins'kyi, *FKhTT* **10** No 4, 957 (2009).
6. I. Ayerdi, E. Castano, A. Garcia-Alonso, F.G. Grasia, *Sensor. Actuat. A-Phys.* **46-47**, 218 (1995).
7. G.-S. Chung, *Sensor Actuat. A-Phys.* **135**, 355 (2007).
8. S.S. Gorelik, L.N. Rastorguev, Y. Skakov, *X-ray and electron graphical analysis of metals* (Moscow: GNTI: 1963) [in Russian].
9. K. Nakamoto, *Infrared and Raman Spectra of inorganic and coordination compounds* (Moscow: Mir:1991) [in Russian].
10. S. Rani, J. Shanthi, *Int. J. Sci. Res.* **3** No 2, 320 (2014).
11. K. Srinivasa Rao, B. Rajini Kanth, P.K. Mukhopadhyay, *Appl. Phys. A-Mater.* **96**, 985 (2009).
12. F. Guinneton, L. Sauques, J.C. Valmalette, F. Cros, J.R. Gavarri *J. Phys. Chem. Solids* **62**, 1229 (2001).