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RESEARCH OF ACIDITY OF THE SURFACE OF POWDERS AND PROPERTIES OF THIN FILMS OF Ta_2O_5 – La_2O_3 SYSTEM, OBTAINED BY SOL-GEL METHOD

V.V. Kozik, O.V. Liseenko, L.F. Ikonnikova, L.P. Borilo

Tomsk state university
E-mail: borilo@mail.ru

Thin films and powders of Ta_2O_5 – La_2O_3 systems are obtained by sol-gel technology. The physical and chemical properties of the synthesized films: adhesion, electric resistance, thickness, coefficient of refraction and acidic-basic properties of the powder surface are investigated. Diagrams of the condition «composition – coefficient of refraction, surface acidity» are built.

Research and regulation of physical and chemical surface properties of solids obtained by sol-gel method, as well as studying of depth and direction of the processes proceeding with participation of a formed solids phase, is the important problem of applied chemistry. Stability of fastening of films on a surface, optical and physical properties of films define possibility of their practical use. The acidic-basic properties are universal physical and chemical criterion of a solids surface which depends on chemical nature of substance, way of its preparation, chemical composition of system and quantity of impurity on a surface, therefore studying of these characteristics is the actual problem for thin films, too. In this connection these properties of thin films and disperse powders of the Ta_2O_5 – La_2O_3 system obtained by sol-gel method were studied in this work.

Experimental part

Samples of the Ta_2O_5 – La_2O_3 system with La_2O_3 contents from 0 up to 100 mol. % have been obtained by sol-gel technology from the film-forming solutions [1]. The film-forming solutions have been prepared by dissolution $TaCl_5$ and $LaCl_3 \cdot 7H_2O$ in dried ethanol. The films have been obtained on the MPW-340 centrifuge with rotation speed 2500 rot./min. As substrates one used single crystalline silicon of КЭФ-10 mark. Thermal processing of the films after preliminary drying at 333 K was carried out in a muffle furnace at temperature 873 K. Composition of films and powders was defined with the ДРОН-3М diffractometer, CuK_α-radiation (λ=1,5418 nm); Ni-filter. Adhesion of films to a substrate was measured with the ПМТ-3 hardness microtester. Index of refraction and thickness of oxide films

were investigated with the ЛЭФ-3М laser ellipsemeter. Physical properties of the films (surface resistance, energy of activation of charge carriers) were studied with the E6-13A teraohmmeter with the help of the B7-40 voltmeter in the air atmosphere and in the temperature interval 293...673 K (clamping Pt-contacts). To study morphology of obtained film surface the SEM-515 scanning electron microscope (accelerating voltage – 30 keV) was used in the work. Simultaneously the samples of disperse powders the Ta_2O_5 – La_2O_3 system to be researched were prepared for which the acidic-basic properties of surface were investigated, by pH value of water suspensions ($pH_{initial\ water}$=7,0) through 2 h of contact in «solids – water» system ($pH_{susp.2h.}$) [2]. An establishment of pH_{susp} was fixed on the «ЭВ-74» universal ionometere with glass electrodes.

Results and discussion

Surface resistance of the obtained films is in range of 10^{11}...10^{13} Ohm.cm. The film have approximately identical thickness on all surface of a substrate being 50...40 nm. High values of adhesion (8,5...7,8 MPa) testify to good adherence of the films of Ta_2O_5 – La_2O_3 system with a substrate. It confirms in turn occurrence of chemical bounding between oxide films and the silicon substrates with thin surface layer of silicon dioxide .

Microscopic researches of the films of Ta_2O_5 – La_2O_3 system show, that the films are on the whole poreless, continuous, and uniform.

For the system being researched the diagram composition – property, Fig. 1 where as property the structural – sensitive parameter – coefficient of refraction is taken, is built. As one can see from the diagram (fig. 1, *б*), coefficient of refraction changes by uneven way in dependence on the film composition and has extreme points 2,05; 2,03; 1,98 at ratio Ta_2O_5:La_2O_3 – 5:1; 3:1; 1:1, accordingly. Results of the X-ray phase analysis of the researched thin films have shown, that at such ratio the chemical compounds with structure $LaTa_5O_{14}$, $LaTa_3O_9$, and $LaTaO_4$. are formed.

The acidic-basic parameter as well as a index of refraction of the films was used for construction of the composition – property diagram. The values $pH_{susp.2h.}$ for samples with different ratio Ta_2O_5:La_2O_3 after approach of balance during 2 h are given on the diagram, Fig. 1. It is seen on the acidity diagram (Fig. 1, *а*), that the additive of lanthanum oxide (III) having the more expressed basic properties in tantalum oxide (V), results in decrease of acidity of sample surface.

Research of acidity of powder surface shows, that experimental data of values $pH_{susp.2h.}$ change from 6,7 to 9,1 (Table). So, the samples consisting on 100 % from Ta_2O_5, have acid character, on kinetic curve of suspension acidity within the first 30 minutes of contact (Fig. 2) it is observed gradual decrease of $pH_{susp.}$ from 7,1 to 6,7 which remains constant during 2 h. At introduction in system of 8 mol. % of lanthanum oxide (III) acidity of the sample also decreases on 0,2 units ($pH_{susp.2h.}$ changes from 6,7 up to 6,9). The further increase of the content of lanthanum oxide (III) results in increase of value $pH_{susp.2h}$ up to 9,1 for 100 % La_2O_3. At this time of establishment of stable value $pH_{susp.}$ are reduced down to 5 min for 100 % La_2O_3 (fig. 2). Thus, the surface of samples has acidic properties at content of La_2O_3 up to 16,7 mol. % and the basic properties – at contents of La_2O_3 in system above 16,7 mol. %.

Also it is possible to note, that on the diagram of acidity extreme points are observed at some contents of lanthanum oxide (III) in samples above 16,7 mol. % which coincide with extreme points on the diagram of fusibility and light refraction (fig. 1). Extreme points on diagrams «structure – property» characterize the special state of the system (eutectics and chemical compositions). Formation of chemical compounds in the Ta_2O_5 – La_2O_3 system is confirmed in addition to the X-ray phase analysis, by the data of the thermal analysis. The sharp increase of value $pH_{susp.2h.}$ is connected with formation of chemical compounds. At content of 25, 50, 75 mol. % La_2O_3 in samples acidity of powders sharply decreases on the average on 0,7 units of pH ($LaTa_5O_{14}$ pH=7,1; $LaTa_3O_9$ pH=7,8; $LaTaO_4$ pH=8,5; La_3TaO_7 pH=9,0). In eutectic points value $pH_{susp.2h}$ is less than in points of formation of chemical compounds as the mechanical mix of two oxides is formed. More acidic surface of mechanical mixes in relation to one of chemical compound samples can be explained by mutual influence of elements (tantalum and lanthanum). As acid properties of tantalum are higher (the V-th Group of the Periodic system), than ones of lanthanum (the III-th Group of the Periodic system) acidity of a mechanical mix of oxides in the Ta_2O_5 – La_2O_3 system naturally decreases.

Change of $pH_{susp.2h}$ of the samples which composition is between points of formation of chemical compounds and eutectics of acidity diagram, proceeds linearly. Linear sites of change pH are corresponded by liquidus fields of fusibility diagram of the system (fig. 1, *в*), that testifies to simple summation of acidic-basic properties of the system due to increase of concentration of one of phases of two-component system. Judging from coincidence of bend points of a curve of acidity change of researched structures from composition with extreme points on the state diagram (fusibility), it is possible to draw a conclusion on essential influence of La_2O_3 phase on acidity of surface of synthesized materials.

The carried out researches have shown, that in the researched system at obtaining of samples from alcohol solutions of tantalum pentachloride, lanthanum chloride and annealing at 873 K, chemical compounds are formed, that is proof not only by classical methods of the analysis of matter structure (X-ray phase and differential-thermal analysis), and also by cioincidence of molar ratio of individual oxides with those on the known diagram of fusibility [3]. The data on surface acidities and index of refraction of thin films can be used for the proof of formation of chemical compounds [4], that is new for the given system. As the estimation of surface acidity by method of pH-measuring ($pH_{susp.2h.}$) is simple, convenient and express the parameter $pH_{susp.2h}$ can be used for construction of the composition – property diagram, and also for characterization of phase condition of system.

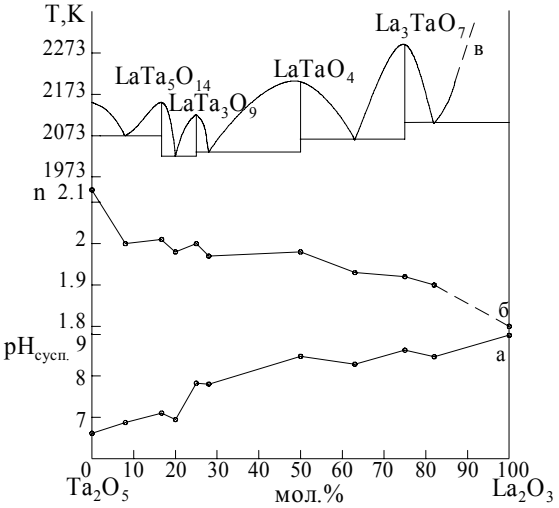

Fig. 1. *The composition – property diagram for the Ta_2O_5 – La_2O_3 system : а) acidity, pH; б) index of refraction n at wave length of measurement 632,8 nm; в) fusibility T, K*

Table. *Change of pH of water suspension of samples for the Ta_2O_5 – La_2O_3 system in dependence on contents of La_2O_3*

Contents of La_2O_3, mol. %	$pH_{susp.2h.}$	Time of stabilization of values $pH_{susp.}$, min
0	6,7	30
8	6,9	28
17	7,1	25
20	6,9	25
25	7,8	23
28	7,8	23
50	8,5	20
63	8,3	16
75	9,0	14
82	8,5	10
100	9,1	5

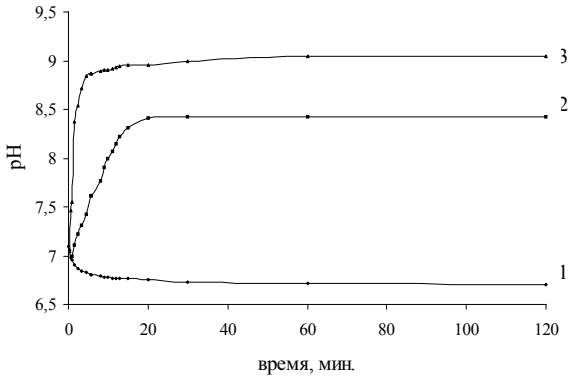

Fig. 2. *Kinetic curve of acidity changes for samples with different contents of La_2O_3, mol. %: 1) 0; 2) 50; 3) 100*

Conclusion

The thin films (40...50 nm) of the Ta_2O_5 – La_2O_3 system on silicon substrates have been obtained from film-forming alcohol solutions. Values of a index of refraction of films for wave length of measurement, 632,8 nm, are changed in interval from 1,93 up to 2,14. Research of surface acidity of the synthesized powders has shown, that in dependence on the contents of lanthanum oxide in samples of the system Ta_2O_5 – La_2O_3 it is possible to obtain complex oxides with $pH_{susp.2h.}$ of surfaces from 6,7 up to 9,1. It in turn enables to synth esize in the given system matters with different type of surface-active centres. It is established, that acidity of a surface of the powders obtained from film-forming solutions, also are changed in steps in dependence on phase condition of the system. In this connection the given parameter can be used, as well as index of refraction, for construction of the «composition – property» diagram.

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