

Acid-Base Properties Of Glass Substrate And $\text{SiO}_2 - \text{Bi}_2\text{O}_3$ Thin-Film Systems Obtained On It

A G Mal'chik^{1,a}, S V Litovkin¹, A V Filonov¹, O V Ulyanova^{1,b}, V E Gromov^{2,c}

¹ Yurga Institute of Technology (branch) National Research Tomsk Polytechnic University, Leningradskaya st. 26, Yurga, Russian Federation, 652055

¹ Siberian State Industrial University

Kirova st. 42, Novokuznetsk, Russian Federation, 654007

E-mail: ^aale-malchik@yandex.ru, ^bolgauljanova@mail.ru, ^cgromov@physics.sibsiu.ru

Abstract. The article describes an experimental research as a result of which $\text{SiO}_2 - \text{Bi}_2\text{O}_3$ films have been synthesized of film-forming solutions based on tetraethoxysilane and bismuth nitrate (III). Acid-base properties of a glass substrate and $\text{SiO}_2 - \text{Bi}_2\text{O}_3$ films obtained on it have been studied. The dependency of physical and chemical properties of $\text{SiO}_2 - \text{Bi}_2\text{O}_3$ composites on their percentage composition have been revealed.

Introduction

Efficient use of resources is the main task of the world community. First and foremost Resource conservation implies ensuring the most effective environmental management, choosing the best way of reproduction and protection of natural resources, taking into account environmental factors when solving economic problems. We should address such problems as advanced processing of natural raw materials and of industrial and consumer wastes, introduction of waste-free or low-waste resource and energy efficient technologies and environmentally friendly production, prolonging service life of equipment and its separate parts [11]. Many of these problems can be solved by obtaining and using new materials with desired properties, thin films and nanopowders being among them [8]. In this view it is important to study and control physicochemical properties on the surface of solids, to identify active centers responsible for its reactivity as well as for the depth and direction of solid phase processes [1,6]. One of important physicochemical characteristics of a solid surface is an acid-base parameter which depends on the nature of the substance, its preparation method, chemical composition, nature and amount of impurities on the surface [4]. The aim of this work is to study physical and chemical processes underlying properties and synthesis of thin films and to obtain thin films of $\text{SiO}_2 - \text{Bi}_2\text{O}_3$. The work investigates the acid-base properties of a glass substrate and studies physicochemical properties of the films obtained.

Experiments

To obtain thin-film systems with a predetermined composition film-forming solutions (FFS) made of 96% ethanol, tetraethoxysilane, bismuth nitrate. The films were prepared on silicon and glass substrates. Two methods were used for obtaining the films: centrifuging at the rate of 3000 - 5000 rev / min and drawing at the rate of 1 - 5 mm/s. The samples were incubated at a temperature of 333K for 30 minutes. The final film formation was performed at a temperature of 873 K for an hour. The



refractive index and thickness of the films were measured at 5 points of each sample using a laser ellipsometers LEF-3M and "SE400advanced". The phase composition of the films was studied with the help of DRON-3M diffractometer (using CuK α -radiation and at a shooting rate of 2 deg / min.). Acid-base properties of solid surfaces were determined by means of ion exchange adsorption using a pH-meter of pH - 673M type, as well as by spectrophotometric version of indicator method on the SF-20 spectrophotometer.

Discussion

SiO₂-Bi₂O₃ system is promising in terms of creating a gas-sensitive elements [9,10]. The presence of differently charged cations indicates a change in the adsorption and resistive properties. Analysis of the surface acidity found that in this system it is possible to obtain compound oxides with surface pH from 2.5 to 9.5 depending on the content of bismuth oxide in the samples and the firing temperature. This variation allows obtaining a substances with different types of surface-active centers. So the samples dried at 333K are strongly acidic on the surface. Data of samples total acidity are presented in Table 1.

Table 1 - Total acidity of samples SiO₂ – Bi₂O₃

Bi ₂ O ₃ content, % mole	Sample acidity	
	Dried at T=333K	Fired at T=873K
0	–	5.40
10	2.49	5.40
20	2.11	5.50
30	1.95	5.80
40	1.75	6.40
50	1.70	7.05
60	1.68	7.46
70	1.66	7.49
80	1.5	7.49
90	1.48	–
Pure substrate	–	8.3

Figure 1 shows the dependence of surface acidity of SiO₂-Bi₂O₃ system samples on bismuth oxide (III) content. When the content of bismuth oxide in the system increases up to 30-35% surface acidity of the sample increases sharply (pH_{susp} decreases). When the content of bismuth oxide is more than 35% the acidity remains practically unchanged. The time of adsorption-desorption equilibrium stabilization changes symbatically with change in the acidity.

Annealing of the system at 873 K increases the pH_{susp} values (Figure 1, curve 2). The surface of the samples acquires weak acid properties when Bi₂O₃ content is not more than 30% and weak base properties when it is more than 60%. Values of surface acidity of samples consisting of 100% of SiO₂ and Bi₂O₃ indicate that if the mass fraction of Bi₂O₃ in the system is below 30% , there are no significant quantities of Bi₂O₃, to affect the density of the samples. When the content of Bi₂O₃ in the system is more than 30% of a composite structure SiO₂-Bi₂O₃ is being rapidly developed. Thus compounds of varying composition mSiO₂:n Bi₂O₃ are generated.

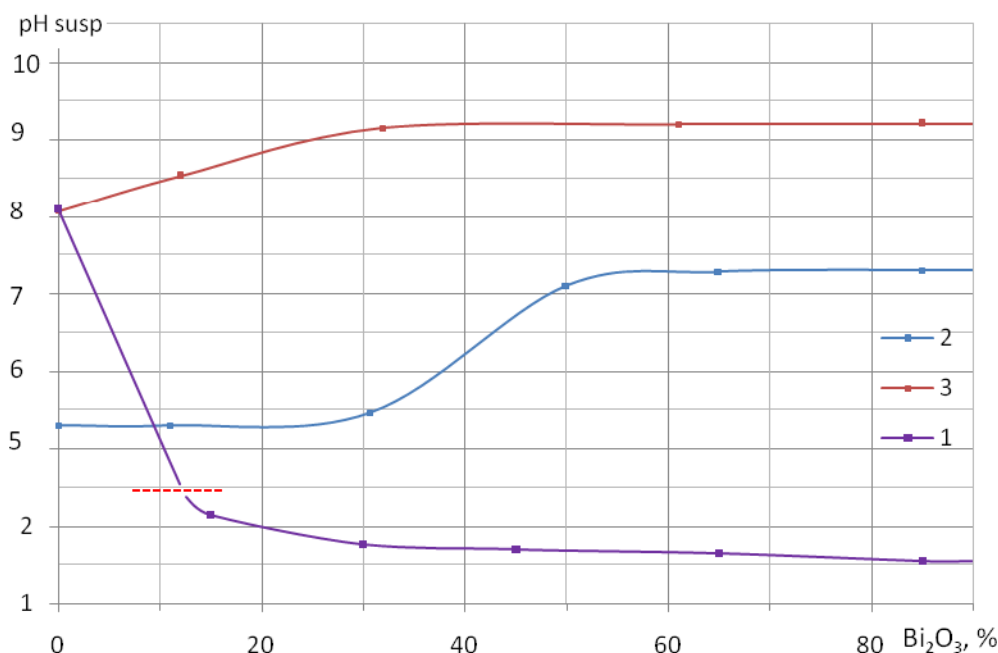


Figure 1 – Dependence of surface acidity of SiO₂-Bi₂O₃ samples on bismuth oxide (III) content. (1 – dried at 333K; 2 - annealed at 873K; 3 – three layer surface annealed at 873K)

Equal weight percentage interval of mSiO₂:nBi₂O₃ system (less than 30%, from 30% to 60%, and more than 60%) in which the change in samples acidity and eutectic state occur indicate correlation of the two parameters: the higher Bi₂O₃ concentration in a sample, the less acidic it is. Thus an intensive generation of a composite material with a high content of Bi₂O₃ is taking place. Moreover, increased concentrations of Bi(NO₃)₃•5H₂O in the system of film-forming solutions (FFS) based on tetraethoxysilane (TEOS) and Bi(NO₃)₃•5H₂O lead to increase in the temperature at which the materials are generated.

Decrease of the eutectic temperature in the film-forming solutions system Si-Bi-O is associated with generation of film-forming solutions of intermediate organic associates. So, matching of the curve break points showing changes in the acidity of the samples depending on their composition with eutectic points proves a decisive influence of Bi₂O₃ phase on the surface acidity of the synthesized film structures.

As mentioned above, decrease of the object acidity from pH = 5.5 to pH = 7.5 is consistent with amphoteric properties of Bi₂O₃ in the presence of SiO₂.

According to acidity changes, drying does not lead to Bi₂O₃ phase in the entire investigated content interval. The surface of the objects is strongly acidic in nature due to Bi nitrite occurrence in polycondensed silicone compounds.

Annealing at 873 K causes decomposition of bismuth nitrate and generation of silicate Bi, as evidenced by the decrease in acidity from pH = 2 to pH = 5.5. Increase in the mass content of bismuth oxide (III) up to 30% does not lead to changes in surface acidity. This also corresponds to the state chart data. A further increase in concentration induces a sharp decrease of acidity and is due to 2Bi₂O₃•3SiO₂ phase developed in all the samples. When the mass fraction of Bi₂O₃ is 60% pH is being stabilized and is close to bismuth oxide surface acidity of pH = 7.5.

Another dependence of sample surface acidity on the SiO₂: Bi₂O₃ ratio can be observed when the samples are applied onto a glass substrate. In this case, the surface basic capacity increases drastically in samples containing up to 30% of bismuth and does not change when Bi₂O₃ content is increased (Figure 1, curve 3).

The study of a set of acid-base surface centers by means of an indicator method showed that there is a large number of centers with an acid-base strength of $\text{pH} = 8$. Kinetic curve of acidity changes for the sample in which Bi_2O_3 - 70% is shown as an example of an established equilibrium (Figure 2).

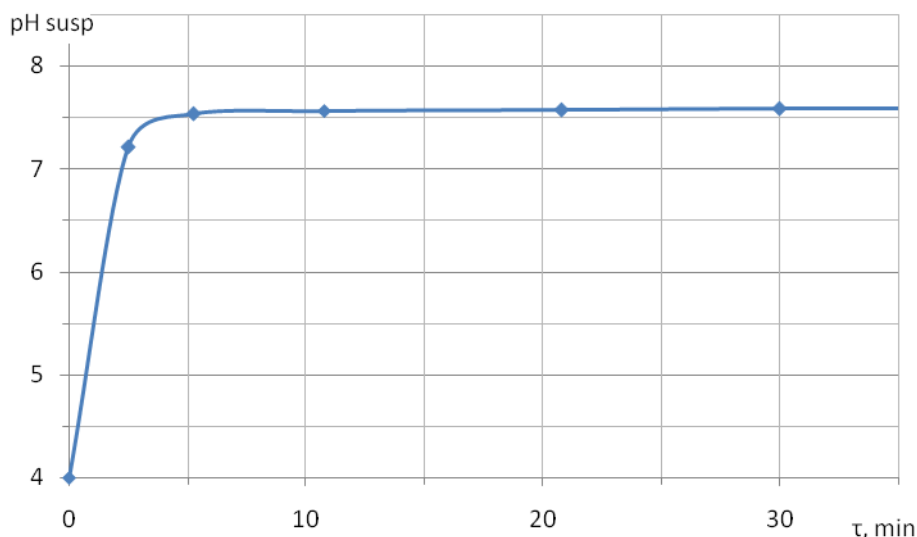


Figure 2 – Kinetic curve of acidity changes in 70% Bi_2O_3 – 30% SiO_2 sample

In the sample composed of 70% Bi_2O_3 - 30% SiO_2 the presence of basic Bronsted centers is proved by differentiation of surface active centers with respect to strength and concentration by means of Hammett method of acid-base indicator adsorption. A dependence of distribution of adsorption centers on the sample surface shows that basic Bronsted centers characterized by $\text{pK}_a = 7$ predominate on the 70% Bi_2O_3 – 30% SiO_2 sample surface but there are also acid centers with $\text{pK}_a = 2.8$ (Figure 3).

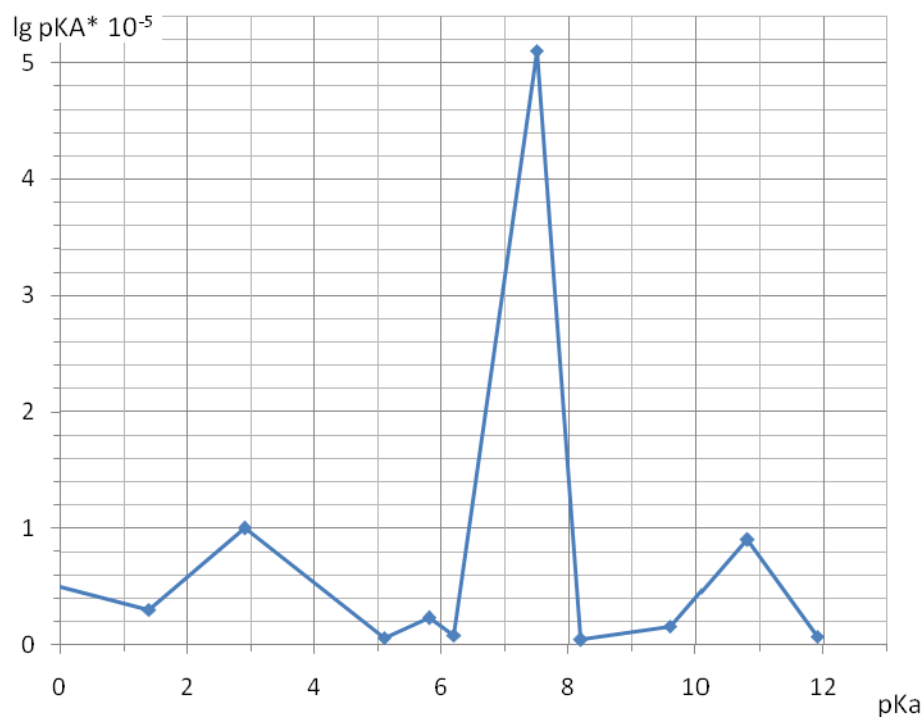


Figure 3 – Distribution curve of acid-base adsorption centers on the surface of 70% Bi_2O_3 – 30% SiO_2 sample

However, the basic centers are ten times more numerous, their number increasing alongside with an increase in Bi_2O_3 content in the system. The nonlinear dependence is stipulated by chemical compounds found in the system. The predominance of the basic centers may be due to the fact that the water proton is attracted to oxygen greater than the hydroxide ion is attracted to Bi^{3+} cation, and the basic centers predominate on the surface [3, 5, 7].

Thin-film structures produced from film-forming solutions containing bismuth and silicon compounds as well as powder materials made from film-forming solutions can be used to create gas-sensing thin-film and ceramic materials for gas sensors.

For films of $\text{SiO}_2 - \text{Bi}_2\text{O}_3$ system, a state diagram showing composition-property relations was constructed in which the property component is presented by a structure-sensitive refractive index (Figure 4).

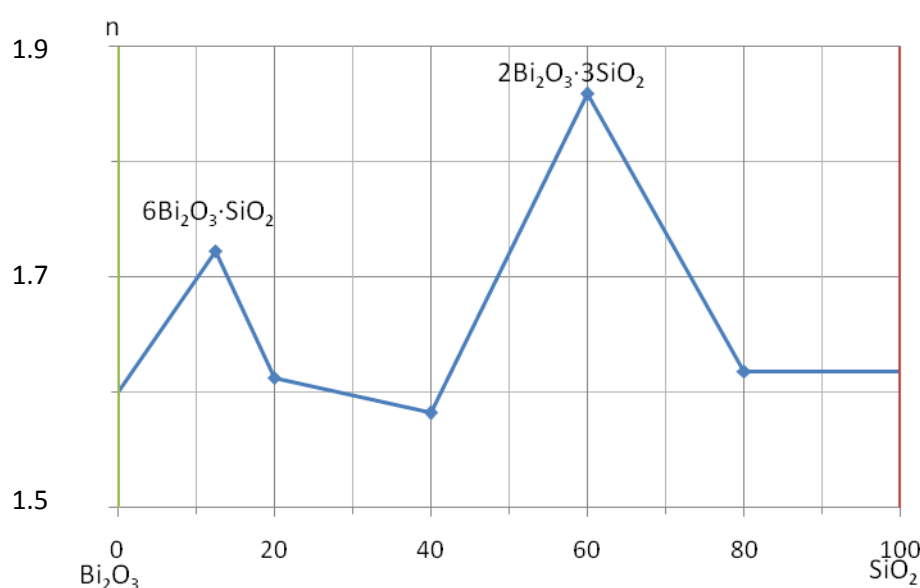


Figure 4 – Composition-property diagram for $\text{SiO}_2 - \text{Bi}_2\text{O}_3$ system

Two data points showing generation of the corresponding silicates ($x\text{SiO}_2 - y\text{Bi}_2\text{O}_3$) are located on the curve, the existence of silicates is confirmed by X-ray analysis (Table 2).

Table 2 - X-ray phase analysis of $\text{SiO}_2 - \text{Bi}_2\text{O}_3$ samples

Compound	d, Å° (theory)	J (%)	2 Θ	d, Å° (experiment)
SiO_2	4.1103	100	30.615	4.1123
	4.0586	60.3	27.16	3.7901
	3.8245	100	50.72	3.8244
	4.2734	100	35.48	4.1975
	1.8211	75.4	60.81	1.5673
	1.0119	20.1	74.44	1.0118
Bi_2O_3	2.6901	100	33.47	2.7508
	2.7631	71.4	32.40	2.6183
	1.6656	33.6	23.5	1.6341
	1.46127	27.0	63.69	1.45607
	1.23483	10.2	77.25	1.23483
	1.21607	23.5	78.69	1.21607
	1.0497	10.7	66.44	1.0372

Compound	d, A° (theory)	J (%)	2 Θ	d, A° (experiment)
6SiO ₂ •Bi ₂ O ₃	1.2103	64.8	42.875	1.2103
	1.7134	70.4	44.75	1.5837
	1.77058	25.5	51.63	1.75046
	1.63347	46.9	56.31	1.62345
	2.1090	64.8	42.89	2.1090
	2.5952	24.5	34.56	2.5952
	1.19606	19.9	80.25	1.2016
2SiO ₂ •3Bi ₂ O ₃	2.7549	100	32.50	2.6958
	3.2008	88	27.19	3.1890
	4.2422	59.7	20.94	4.2003
	4.1329	36.7	21.44	4.0975
	1.5229	24.5	60.81	1.5231
	2.51222	12.8	42.875	2.51171
	1.21607	78.69	23.5	1.3887

Electrical properties listed in Table 3 show that the compounds of SiO₂•Bi₂O₃ system are dielectrics with highly ionic bonds [2].

Table 3 - Physical and chemical properties of SiO₂ – Bi₂O₃ system films

Property	Content of Bi ₂ O ₃ in the film, %								
	10	20	30	40	50	60	70	80	90
Refractive index, n	1.73	1.52	1.50	1.48	1.74	1.85	1.73	1.53	1.53
Dielectric capacity, ϵ	2.43	3.98	4.21	4.62	5.61	4.02	5.83	6.51	7.89
Adhesion strength, F, кг/мм ²	0.99	0.99	0.99	0.98	0.99	0.99	0.98	0.99	0.99

A coating method is of value only if it allows obtaining layers of different materials with a wide range of physical properties to meet technical requirements.

As to the physical characteristics of such films, of the greatest interest are their optical properties, particularly a refractive index and an absorption coefficient. Electrical and chemical protective properties of the films are also important.

High chemical stability and thermal resistance of SiO₂ – Bi₂O₃ oxide films as well as unique technological advantages provided by film-forming solution synthesis allowed the use of SiO₂ – Bi₂O₃ film as protective coatings for miniature incandescent lamps for medicine which have to be resistant to corrosive environments. It is proved that in acidic and alkaline medium, coatings provide light transmittance up to 93% in the visible range and have good dielectric properties [12, 13]. Chemical resistance of the films to water and to corrosive environments is presented in Table 4.

Table 4 - Chemical resistance of SiO₂ – Bi₂O₃ films to water and to corrosive environments

Test conditions		Test results
Environment	Time	
Distilled water	2 years	No changes
Piped water	2 years	Initiation of destruction in 14 months
Acid solution	6 months	Initiation of destruction in 3 months
Alkaline solution	6 months	Initiation of destruction in 4 months

Conclusions

The results of the research let us draw the following conclusions: acid-base properties of a glass substrate and the thin films formed on these structures have been studied, as well as properties of powder materials made from film-forming solutions with addition of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$. It is proved that major Bronsted centers prevail. By means of X-ray diffraction, optical analysis and other methods, relationship between physical and chemical properties of $\text{SiO}_2\text{-Bi}_2\text{O}_3$ composites and their composition have been revealed. Silicate compounds Bi in a thin film form are found to generate. The refractive index of $\text{SiO}_2\text{-Bi}_2\text{O}_3$ films changes in the range from 1.48 to 1.85; film thickness does not depend on the solution ripening time. The films with this composition can be recommended for use as a dielectric coating with high thermochemical stability, which significantly extends the equipment life and meets requirements for resource-saving.

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