Synthesis and Physicochemical Properties of SiO$_2$ – Ta$_2$O$_5$ Thin-Film Systems and Powders

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Abstract. Within the research, SiO$_2$ – Ta$_2$O$_5$ films from film-forming solutions based on tetraethoxysilane and tantalum chloride (V) are synthesized. Physicochemical patterns and specifics of producing the films are determined by means of IR spectroscopy and thermogravimetric analysis. The processes of SiO$_2$ – Ta$_2$O$_5$ films formation are studied. Interrelation between SiO$_2$ – Ta$_2$O$_5$ composition, concentration of incoming components and their physicochemical properties are revealed.

1. Introduction

Many branches of economy use modern ultraviolet technologies such as ultraviolet drying devices, disinfection plants for air, surfaces and water, climatic chambers, weather modification machines, various irradiators for medicine, cosmetology equipment (lamps for hairdressing, manicure, solariums, etc.). Ultraviolet radiation is widely used for industrial and household purposes among which one can find identification of special signs, control of securities, medical, health and cosmetic purposes, etc. [1,2,3].

Excessive ultraviolet radiation can cause a number of diseases and health disorders. These are primarily eye damages including cataracts or clouding of the eye lens, inflammation of cornea and mucous membranes. UV radiation can also lead to skin diseases: inflammatory skin erubescence or erythema, acceleration of skin aging, allergic reactions to UV radiation, skin tumors including skin cancer [4,5].

In this regard, there is a need in various protective technologies to reduce or limit the UV spectrum. Applying a special film on light sources to adjust the UV radiation is one of such technologies. The applied coating is transparent to the required radiation wavelength absorbing the rest parts of the spectrum and thereby reducing the radiation effect.

2. Methodology

To obtain thin-film systems with a given composition, we used film-forming solutions (POR) made from dried ethanol, tetraethoxysilane and tantalum chloride (V). The dried ethanol was used to prevent TaCl$_5$ hydrolysis. The films were produced on silicon and glass substrates. Two production methods were used: centrifugation at a speed of 3000 to 5000 rpm, and drawing at a speed of 1 to 5 mm/s. The samples were incubated at a temperature of 333 K for 30 minutes. The complete filming was carried out at a temperature of 873K for an hour. The refractive index and film thickness were measured at 5 points of each sample using the LEF-3M and "SE400advanced" laser ellipsometers. Phase composition of the films was studied using a DRON-3M diffractometer (using CuKα radiation and a shooting speed of 2 deg/min).

3. Results and discussion

The essence of the oxide film formation is that the chemical composition of initial film-forming compounds undergoes a number of changes: first at the solution stage, then at the moment of film formation on the surface of the substrate and finally during thermal processing. To establish technological conditions for film synthesis, we have studied the main stages of simple oxides and their double oxides formation. Heat treatment reduces concentration of crystal lattice defects, crystal structure becomes thermodynamically more stable which provides stable physical and chemical properties. By changing heat treatment modes and conditions, we can shape the structure and therefore the properties of a product. This problem cannot be solved without a thorough research into kinetics of heat treatment processes [6,7,8].

Thermal gravimetric and IR spectroscopic analysis were carried out for hydrolysed powders dried by thermostating at 333 K. Fig. 1 and 2 show thermogravimetric curves for simple oxides formation.

On the DTA curve (Fig. 1), two endothermic effects are recorded with maxima at 383K and 653K. They are caused by water evaporation from the surface, these processes involving mass loss, the TG curve . The endothermic effect at 653K is caused by evaporation of water generated by condensation of silanol groups when siloxane bonds are being formed. The exothermic effect at 863K is characteristic to combustion of alcohol and high-molecular hydrocarbons to form SiO_2.
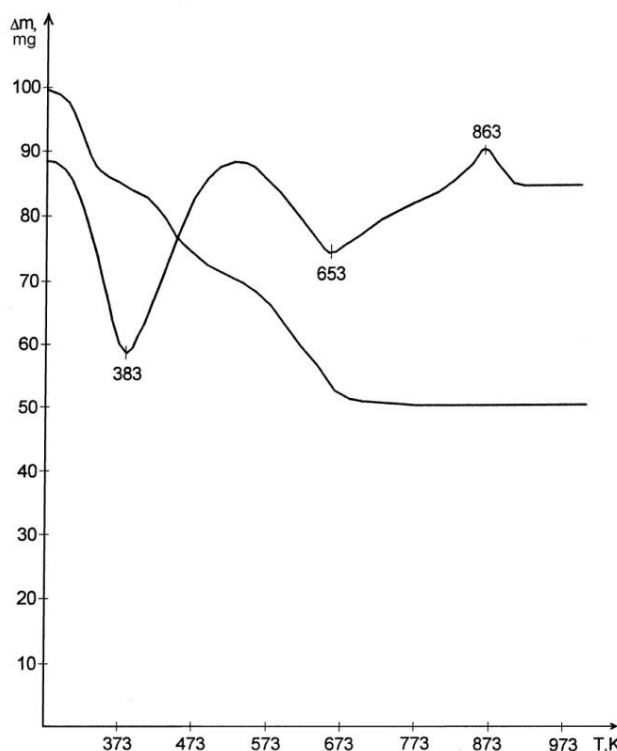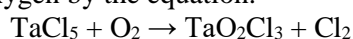

Figure 1. Decomposition derivatogram of film-forming solution dried at 333K.

The DTA curve (Fig. 2) shows that Ta_2O_5 formation also proceeds in three stages. The first stage is involves evaporation of physically adsorbed water and alcohol. At the second stage (exothermic effect at 523K) $TaCl_5$ is oxidized with air oxygen by the equation:

$$TaCl_5 + O_2 \rightarrow TaO_2Cl_3 + Cl_2$$

At the third stage, combustion of oxychlorides and alkoxy derivatives of tantalum takes place to form Ta_2O_5 oxide.
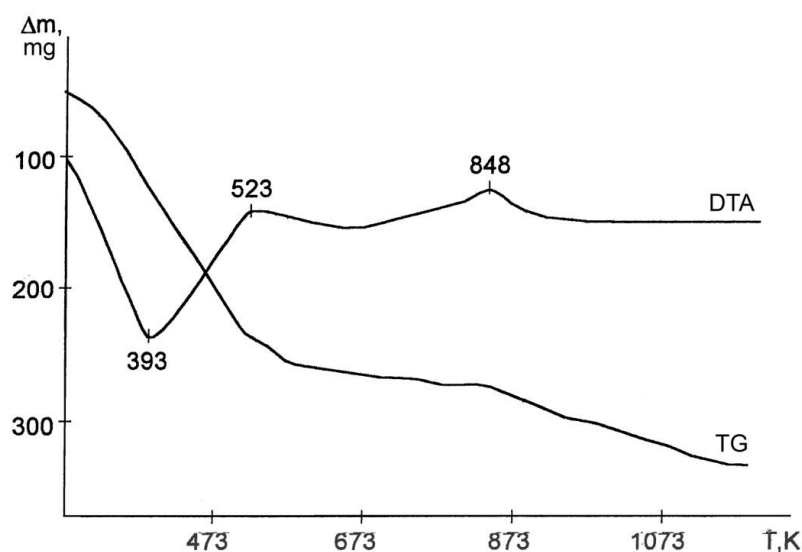
Figure 2. Derivatogram of $TaCl_5$ alcohol solution dried at 333 K

The IR spectra data (Table 1) prove that at 800-840 K there are valence and deformation vibrations associated with ethoxy groups. At higher temperatures, these vibrations do not occur.

The physicochemical processes of double oxides formation are complex. When $SiO_2 - Ta_2O_5$ are formed, the DTA curve shows an effect with a maximum at 393K which coincides with SiO_2 thermal formation effect and corresponds to the processes of polycondensation and physically adsorbed water removal (Fig. 3). The process of $SiO_2 - Ta_2O_5$ complex oxides formation takes place in four stages The exothermic effect at 523K corresponds to $TaCl_5$ oxidation. The processes of bulky ethoxy groups oxidation and $SiO_2 - Ta_2O_5$ oxides formation take place at stages 3 and 4.
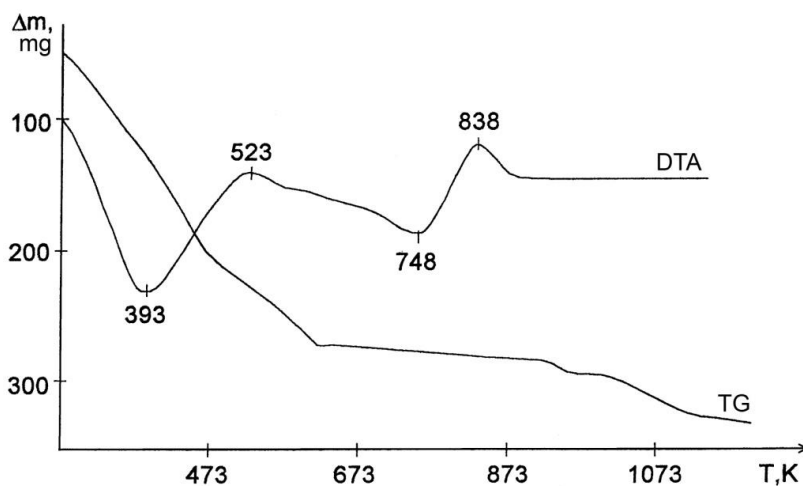

Figure 3. Derivatogram of Ta_2O_5 formation from film-forming solutions with $TaCl_5$

Table 1. Infra-red spectrum bands of powders obtained from
film-forming solutions at various annealing temperatures

Film-forming solution composition; T,K	Vibration type					
	H – OH	Valence –OC$_2$H$_5$	H \ O H/	Deformation –OC$_2$H$_5$	Si – O – Si	O \ Si; O/
TaCl$_5$ + C$_2$H$_5$OH T=373	3600	2900	1640	1200	-	400
T=773	-	2900	-	1100	-	400
T=848	-	2900	-	1100	-	400
T=900	-	-	-	-	-	400
ТЭОС +TaCl$_5$ T=373	3560	-	1640	1000	600-800	460-400
T=600	3600	2900	1640	1000	600	460-400
T=633	-	2900	-	1100	600	460-400
ТЭОС + C$_2$H$_5$OH T=373	3660	2935	1640	1095	600-800	460
T=473	1380	2935	1640	1100	800	460
T=773	-	-	-	1100	800	460

Process activation energies are calculated for each stage, the data are summarized in Table 2. The activation energy of the first process, E = 41.3 kJ/mol, agrees with these values for condensation of hydroxyl-containing organosilicon compounds [9,10,11].

Table 2. Kinetic parameters for f SiO$_2$, Ta$_2$O$_5$ and SiO$_2$ – Ta$_2$O$_5$
powders production (according to thermogravimetric and DTA methods)

Formation stage	Powder SiO$_2$			Powder Ta$_2$O$_5$			Powder SiO$_2$ – Ta$_2$O$_5$		
	T interval, K	Degree of transformation, %	E$_a$, kJ/mol						
	1	2	3	1	2	3	1	2	3
1	298-473	33.0	41.4	298-473	51.7	44.1	298-473	50.0	40.5
2	473-623	29.0	51.8	473-573	15.0	32.1	473-623	34.5	32.6
3	623-973	37.5	68.5	573-923	33.3	107.8	623-763	3.4	60.9
4							763-973	12.0	117.4

The research data prove that it is possible to control the film synthesis by changing concentration of incoming components and process conditions. Obtaining films of a certain thickness and with given physical and chemical characteristics can be provided only by using high quality film-forming substances and properly prepared solutions and by following the processing methods.

Based on the results of the research into physical and chemical properties of film-forming solutions, we have developed a technology for preparing solutions to produce homogeneous films of SiO$_2$ – Ta$_2$O$_5$ systems.

Coatings produced from these solutions can form complete glassy films which have a number of valuable qualities. The surface holding power of the films as well as their optical and electrophysical

properties make their practical use efficient. The research showed that the obtained films have good adhesion to various substrates and are nonporous.

Optical, electrophysical and adhesion properties of $SiO_2 - Ta_2O_5$ films have been studied (Table 3). The refractive index changes linearly from 1.45 (for SiO_2) to 1.98 (for Ta_2O_5) (Fig. 4), which indicates there are no chemical compounds in this system and a mechanical mixture of oxides is formed similar to bulk samples state diagram [12,13].
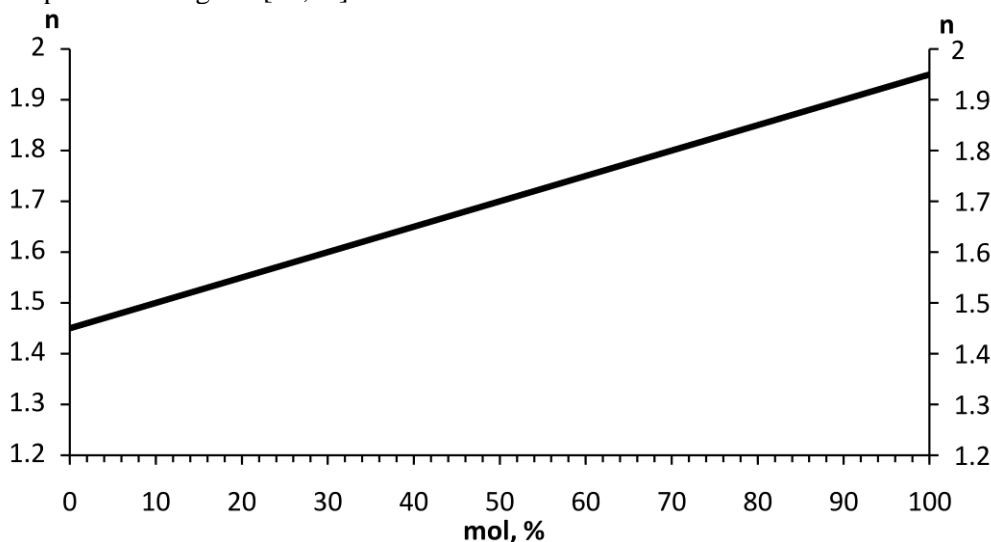

Figure 4. Dependence of $SiO_2 - Ta_2O_5$ film refractive index on Ta_2O_5 content

Table 3. Physical and chemical properties of $SiO_2 - Ta_2O_5$ films

Properties	Ta_2O_5 content in films, %								
	10	20	30	40	50	60	70	80	90
Refractive index, n	1.51	1.61	1.63	1.63	1.69	1.72	1.75	1.83	1.91
Dielectric permittivity, ε	4.6	5.1	7.4	9.2	11.0	12.5	14.3	15.1	16.5
Adhesive power, F, kg/mm^2	0.93	0.95	0.91	0.96	0.97	0.94	0.96	0.94	0.95

Electrophysical properties show that SiO_2-Ta_2O_5 films are dielectrics (Table 3) which have a lower dielectric constant but a smaller loss angle (tg = 10-3) in comparison with pure Ta_2O_5. Small *tg* values speak for either a defect-free film structure or a structure with very uniform defectiveness.

A coating method can be assessed an efficient one only if it provides obtaining layers of different materials with a wide range of physical properties to meet engineering requirements. Film optical properties (refractive index and the absorption coefficient) are the most significant of their physical properties. The problem of regulating and filtrating optical radiation in the ultraviolet spectrum is important for various fields of technology. Using light-redistributive UV-radiation coatings for high-intensity light sources is of particular interest [14,15].

Figure 5 shows optical transmittance spectra of SiO_2 and Ta_2O_5 films. Since optical properties of films depend on their molecular structure, coatings produced from multicomponent solutions have different spectral absorption characteristics from respective one-component coatings. Figure 6 shows transmittance spectra of SiO_2-Ta_2O_5 films of various compositions.
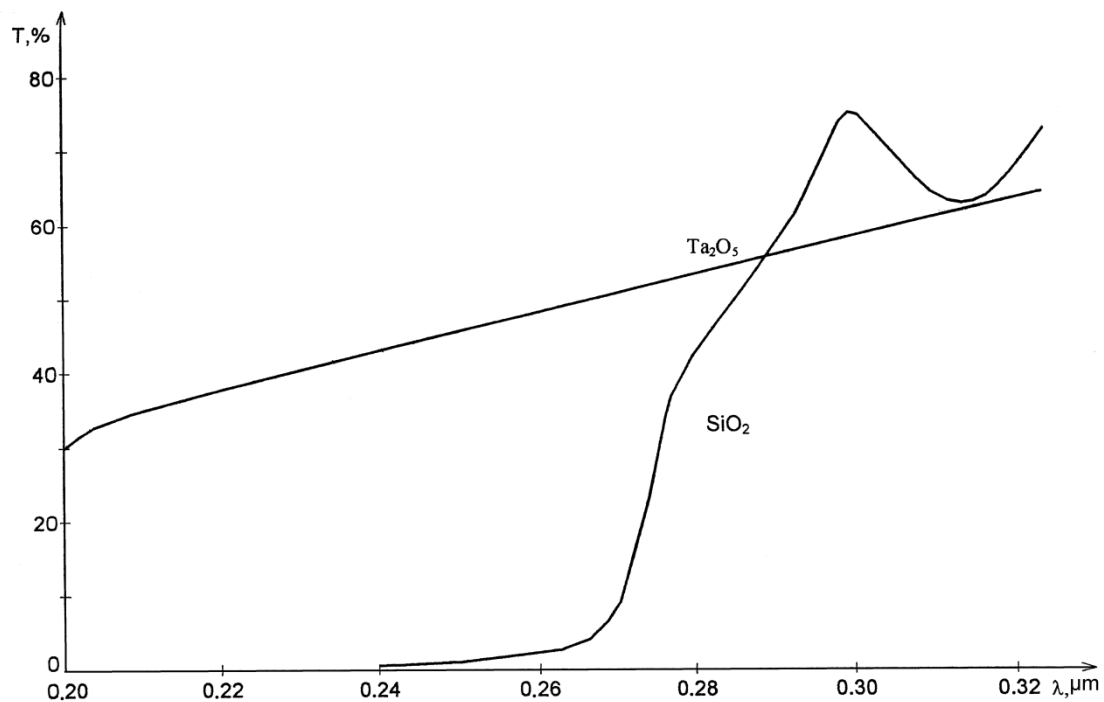
Figure 5. Spectral transmittance of SiO_2 and Ta_2O_5 base films

As can be seen from the optical studies results, when the oxide composition changes from pure SiO_2 to pure Ta_2O_5, the absorption wavelength is in the range of 160 to 300 nm. The research prove that it is possible to control λgr depending on the oxide.
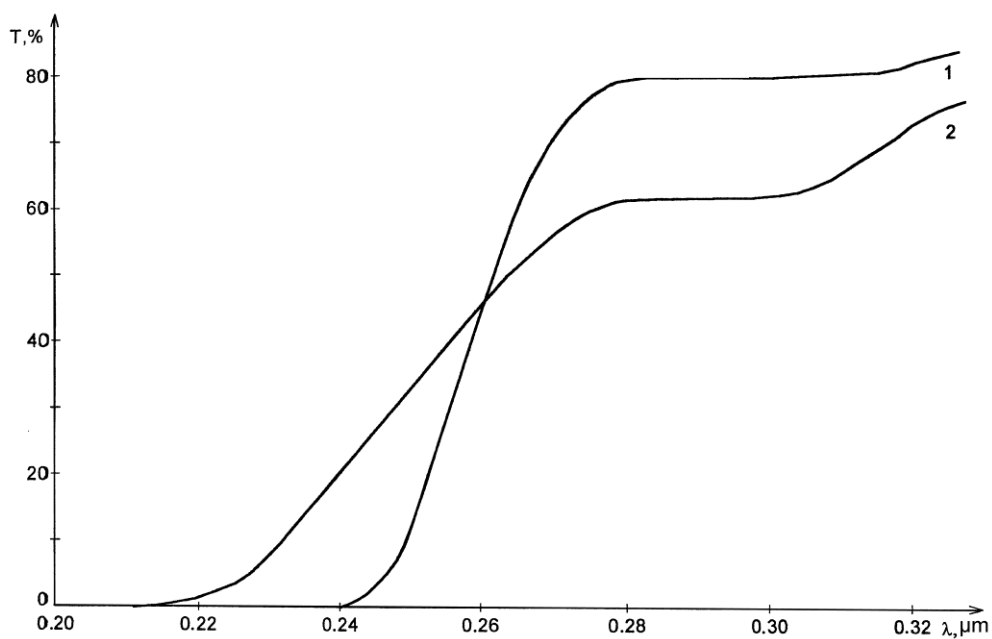

Figure 6. Spectral transmittance of $SiO_2 - Ta_2O_5$ films
1 - 40% Ta_2O_5 concentration; 2 - 20% Ta_2O_5 concentration

Since the operating lamp temperature reaches 770-970K, the thermal stability of the films was evaluated at 670, .870 and 970K. Analysis of transmission spectra showed that λgp position and transmittance do not change at increasing annealing temperature and transmittance index at maximum annealing temperature decreases no more than 10% of the initial one. The results of the study showed that $SiO_2 - Ta_2O_5$ films are of practical interest for correcting ultraviolet spectrum radiated by light sources. Tests of gas-discharge light sources coated with $SiO_2 - Ta_2O_5$ has shown that a film allows reducing ozone generation to 80%. The coating is thermally stabile and does not change the light transmittance index during a light source operation. It is proved that by changing the composition of $SiO_2 - Ta_2O_5$ film it is possible to control the UV radiation transmittance boundary of a gas discharge lamp in the range of 220-300 nm. As a result ultraviolet radiation with a predominantly erythemic, bactericidal or highly inhibitory effect can be generated.

4. Conclusions

A sequence of main formation stages of Ta_2O_5 as well as $SiO_2 - Ta_2O_5$ from film-forming solutions was determined by means of IR spectroscopy and thermogravimetry. Optimal methods of thin-film synthesis were proposed. They consist in preliminary heat treatment at T = 333K and subsequent annealing at T = 873K. Structure and physicochemical properties of the obtained films are analysed. The refractive index for $SiO_2 - Ta_2O_5$ films varies from 1.45 to 1.98. The developed thin-film materials can be used in the production of zero-gap UV radiators with bactericidal and erythemic effect, as well as dielectric coatings of high thermochemical stability.

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