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Article

Development of siloxane coating with oxide fillers for kesteritic (CZTS) photovoltaic systems

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Abstract: The work focused on the development of high-temperature electrical insulation coatings for film photovoltaics. The idea was into replacing the electroconductive metal dispersed phase in siloxane high-temperature coating to ceramic particles with phonon thermal conductivity. The slurry of industrial composition based on polysiloxane lacquer and thermally conductive paste containing zinc oxide was centrifuged to obtain a thin, optically transparent coating with the destruction temperature of over 600 °C. Topology, electrical properties, and thermal conductivity of the resulting film were investigated. The mathematical model of thermal processes in films in the course of heating was figured out. Quantitatively the relation of thermal conductivities of a control sample and a sample with a heat-conducting filler was established. The effectiveness of using this technology is shown.

Keywords: thin-film photovoltaic, the heat-conducting high-temperature isolating coverings, kesterite photoelectric converters.

1. Introduction

Despite steady positions of silicon solar elements (occupy about 90% of the corresponding segment of the world market) the relevance of the development of cheaper thin-film photovoltaic Energy Converter (PEC) [1] at the moment doesn't raise doubts. The thin-film technology has several advantages before silicon analogs. First of all, it is a low consumption of material and rather simple, cost-effective production technology, the ability to efficiently transform to electricity dispelled sunlight and rather a high efficiency (to 20%) and also, a variety of forms and objects of localization of PEC. Deposition of thin-film elements is possible on a surface of any configuration (the surface of the car, glass facades of buildings) that in general, significantly increases the specific area of the functional surface of PEC, reducing at the same time the size of the areas unsuitable for effective economic activity as a result of the placement of PEC [2].

Chemical compounds type kesterite $Cu_2ZnSn(S, Se)_4$ or CZTS(Se) are direct-gap semiconductors with a width of the band gap, optimum for PEC (1.0-1.5 eV) and a high light absorption coefficient (> 104 cm^{-1}). It allows the kesterite type of PEC to convert into electric current the radiation of an optical spectral band with minimum losses at a thickness of only 2-3 microns. As of 2018, the efficiency of CZTS-PEC reached 12.7% [3]. Besides, widespread low-toxic elements in nature are a part of these compounds that in turn, resolves an issue of further recycling of solar batteries on their basis [4]. Therefore, PEC-systems based on CZTS(Se) are the most perspective at present and scientific and technological tasks with their development are extremely relevant. One of these tasks is to obtain a dielectric layer for kesterite PEC on a substrate of steel used for roofing. The lack of varnish dielectric polymer materials withstanding the temperature conditions of the technological process for producing kesterite solar cells is a quite serious problem for deciding the task of electrical insulation of solar cells from the substrate. The coating must withstand for a short time (5–30 min) a temperature regime of 600 °C, be optically transparent, have dielectric properties, and also, have good adhesion to steel and molybdenum.

The most high-temperature polymer – siloxane is chemically stable up to temperatures about 300 °C [5] while the minimum temperature of the process of synthesis of the kesterite is within limits of 500–600 °C depends on the chosen method. Varnishes and enamels based on siloxane are capable to maintain temperatures over 300 °C due to the transfer of heat to a substrate through a heat-conducting disperse phase – the filler. According to the classical concepts of solid-state physics [6–7], electron transfer of heat and charge is the most efficient, so that generally used industrial fillers have excellent metallic-type electrical conductivity. Commonly, it is a fine powder of aluminum or graphite. Their thermal conductivity is within 237 $W \cdot m^{-1} \cdot K^{-1}$ for aluminum and 25-470 $W \cdot m^{-1} \cdot K^{-1}$ for various forms of carbon with an electrical resistance of the order of $5 \cdot 10^{-6}$-$30 \cdot 10^{-6}$ Ω·m (Table 1). Other metal oxides are used as dyes. They do not transfer heat to the substrate, but they have quite good dielectric characteristics (Table 1).

Table 1. Comparative characteristics of the fillers.

Filler	Melting temperature, K	Thermal conductivity W/(m·K), at 300 K	Permittivity at 300 K, in layers, d ≤ 200 nm	Resistance, Ω·m
Powdered aluminium	933 [8]	237 [9]	1,6-1,8 [19]	$2{,}65 \cdot 10^{-8}$ [15]
Carbon (graphite)	4163 [8]	25-470 [10]	10-15 [17]	$5 \cdot 10^{-6}$-$30 \cdot 10^{-6}$ [10]
Fe_3O_4	1867 [8]	4,8 [13]	14,2 [19]	$2{,}05 \cdot 10^{6}$ [18]
TiO_2	2030 [8]	5,8 [9]	40-90 [19]	10^{10} [11]
Al_2O_3	2500 [8]	25-26 [9]	9,5-10 [21]	10^{12} [16]
SiO_2(quartz)	2103 [8]	1,3 [12]	3,8-5,4 [12]	10^{12}-10^{16} [12]
BeO	2803 [8]	272 [9]	7,2 [22]	10^{14} [16]
ZnO	2248 [8]	54 [14]	7,8-8,75 [21]	10^{7}-10^{8} [13]

However, neither of them could be used for solving the task of obtaining high thermal conductivity with extremely low electrical conductivity. The task could be achieved using materials where the phonon heat transfer mechanism is effective but the electron mechanism is reduced. Materials having suitable characteristics include beryllium oxide (thermal conductivity 272 $W \cdot m^{-1} \cdot K^{-1}$, electrical conductivity $8 \cdot 10^{-13}$ – $4 \cdot 10^{-1}$ $\Omega^{-1}cm^{-1}$ [23]), and undoped zinc oxide (thermal conductivity 54 $W \cdot m^{-1} \cdot K^{-1}$), electrical conductivity 10^{-8}–10^{-10} $\Omega^{-1}cm^{-1}$ [24]), have relatively long used in electronics. The working concept of this research is the replacement of metal and carbon fillers in industrial varnishes for a non-conducting filler with good heat conductivity.

The objectives of the study include: obtaining components of polymer coatings from well-known industrial products (High-temperature enamel and heat-conducting paste KPT-8); obtaining a highly dispersed emulsion of the components of polymer coatings with the desired viscosity; working off a technique of composition applying to the surface; study of thermal resistance and electrical strength of the coatings.

Films were obtained by using spin-coating at a shaft rotational speed of 1200 rpm for 1 s.

2. Materials and Methods

As a substrate polished cuttings of low-grade sheet roofing steel (GOST 8075—56) were used by size 30x15mm. As a polymer base, - siloxane varnish used in the composition of the silicone heat-resistant enamel "DALI", (GOST TU 2312 - 114-13238275 - 2013) was used. Zinc oxide powder according to GOST 202-84 of the BTs0 and BTs1 grades in the composition of heat-conducting paste KPT-8 (GOST 19783-74) was used as a filler. Powder separately wasn't emitted from this paste because it is made on the organic silicon polymeric basis compatible with the used varnish.

The surface of the obtained films was investigated by the method of profilometry on the device MicroSpy® FT. Optical microscopy was performed using a Digital Microscope Electronic Magnifier digital microscope. Differential scanning calorimeter DSC 204 F1 Phoenix with NETZSCH μ-sensor was used to study the thermal strength of the samples. Electrical measurements were performed using a VC9808 precision multimeter.

The research of thermal properties was conducted by direct heating of a film surface on a metal substrate by the dryer in a temperature range of 50 - 600 °C. At the same time, the substrate had thermal contact with a heat-removing basis that allowed it to obtain a heat conductivity gradient. Heating duration on each point was 10s, a step of temperature increasing – 50 ° C. Temperature difference of a film on the side of the open surface and the side of the substrate was defined using two thermocouple instruments for thermal measuring based on a chromel–alumel alloys and two VC9808 devices.

3. Results

3.1. Microstructure and electrical properties

Data of the optical microscopy are presented in Figure 1. The contrast in the right part of the image is the transition between the surface of the film and the ground surface of the metal can be seen. The film with filler has a light-dairy shade. The effect of reducing heterogeneities as a result of filling with varnish grooves in the metal can be noticed.

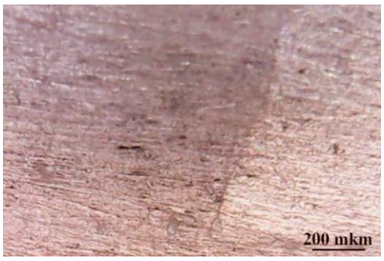

Figure 1. Optical microscopy (magnification x500) varnish / xylene / filler KPT-8: 10/10/1 film.

The electrical resistance of both types of films exceeds the limit of the range of used measuring devices and is more than 2000 MΩ. Therefore, at the synthesized heat-conducting films the leakage current doesn't exceed 10-9A. At operating currents of an element about 100 mA, this makes a value no more than 10-3%. Thus, the received films are dielectrics.

The topology of the film surface at the microscopic level is presented in Figure 2. The data of profilometry demonstrate the good distribution of a covering on a substrate: the film is homogeneous and smooth. The difference of heights in the explored area makes order size 16-18 μm and is probably defined by a technique of suspension deposition and its rheological characteristics.

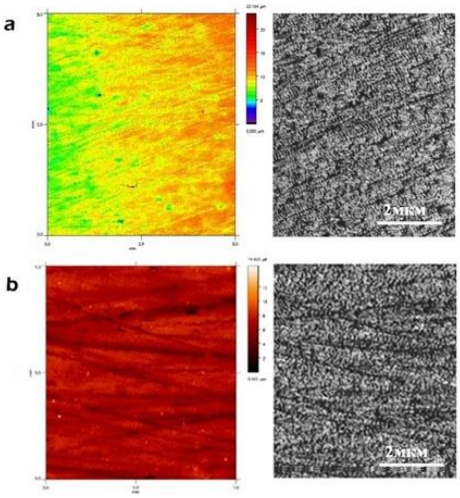

Figure 2. Height profiles in films without filler (a) and with ZnO filler (b).

Differential Scanning Calorimetry (DSC) results are presented in Figure 3. The temperature (°C) is shown on the Abscissa axis and specific heat absorption power (mW/mg) on the Ordinate axis.

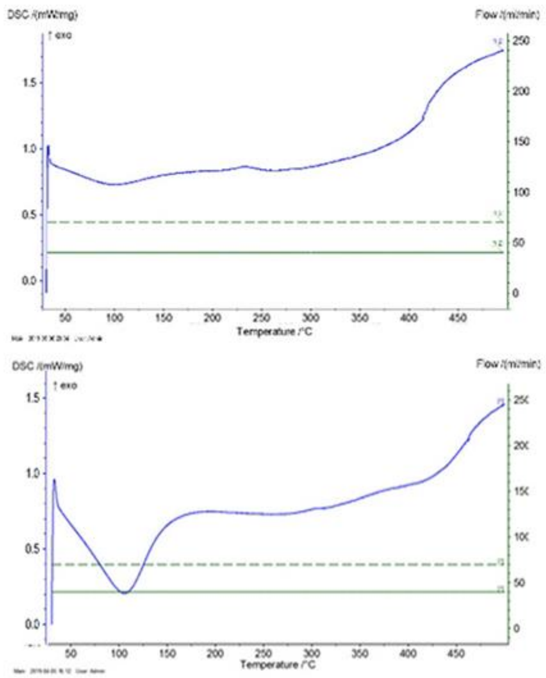

Figure 3. The DSC curves of the varnish/xylene: 1/1 film composition (a) and the varnish/xylene/KPT-8 filler: 10/10/1 composition (b).

Apparently, from Figure 3a, the process of a glass transition of polysiloxane filler without excipient occurs in a temperature range: 402 - 422° C.

A similar result is obtained in the case of varnish filled with ZnO (Figure 3b). Consequently, in the case of using quasistatic heating at a speed of 20 °/ min, the filler does not lead to a significant change in the temperature stability of the siloxane coatings.

To determine the effectiveness of ZnO - filler in increasing resistance of the film to thermal influence, the most appropriate experimental approach is a measuring of a temperature gradient at heating in this case. According to the base assumption, the filler will reduce the degree of overheating of the film by increasing the efficiency of heat removal to the substrate.

3.2. The study of thermophysical characteristics. Mathematical description of thermophysical processes in the studied system.

A boundary value problem about the heat conductivity of a flat wall at boundary conditions of the first kind was used for mathematical descriptions of the processes of heat conductivity in the studying films upon heating. Heat conduction processes are described by the equation which in this case has an appearance of a differential equation (1). In case of quasistationary conditions (heating was made periodically, within 10 seconds most of the time t, in the absence of internal sources of warmth) the differential equation of heat conductivity of this system has a form:

$$\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2} = 0, \quad (1)$$

If to assume that temperature changes only perpendicular to the substrate plane, then $\frac{\partial^2 T}{\partial y^2} = 0$, $\frac{\partial^2 T}{\partial z^2} = 0$ and the differential equation can have the following look:

$$\frac{\partial^2 T}{\partial x^2} = 0, \quad (2)$$

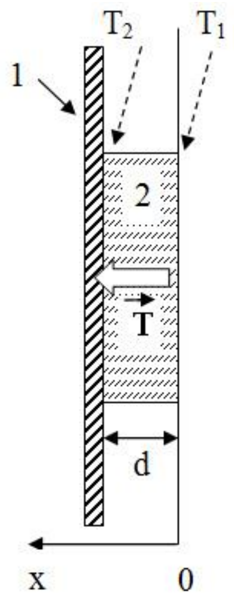

Figure 4. Graphical representation of the conditions of the boundary value problem to be solved, where:

1 - the substrate collector of thermal energy;

2 – the film through which the heat flux passes,

T_1 and T_2 - the film temperatures from the upstream side of heat flux and a substrate;

d - the thickness of the film;

T - the direction of propagation of the heat front;

x - the spatial coordinate (the normal to the platform through which is carried out heat transfer)

The heat transfer equation for the system under study received by integrating equation (2) and has a form:

$$\frac{\partial T}{\partial x} = C_1; \quad T = C_1 x + C_2 x, \quad (3)$$

where C_1 and C_2 - some constants characterizing the process of heat exchange between a film and a substrate.

There are next initial boundary conditions: d = 10 – 50μm (layer thickness), $T = T_1$ at $x = 0$, $T = T_2$ at $x = d$ find C_1 and C_2:

at $x = 0$: $T = T_1 = C_2$;

at $x = d$: $T = T_2 = C_1 d + C_2$.

Then:

$$C_1 = -\frac{T_1 - T_2}{d}, \tag{4}$$

and

$$T = T_1 - \frac{T_1 - T_2}{d}x, \tag{5}$$

An equation of motion of the temperature front received by substituting of Equation 4 in Equation 3:

$$\frac{\partial T}{\partial x} = -\frac{T_1 - T_2}{d} = -\frac{\Delta T}{d}, \tag{6}$$

4. Discussion

Determination the quantitative parameters of the effectiveness of the filler.

In Figure 5, temperature dependences of the temperature gradient in the films obtained without using ZnO filler (curve 1) and using it (curve 2) are presented. It can be seen that the value of the temperature gradient ΔT in the sample volume increases with increasing temperature T, which indicates an increase in heat flux q through the sample with a thickness d:

The Fourier law to determination of the heat flux density q is [25]:

$$q = -\lambda \frac{\partial T}{\partial x}, \tag{7}$$

After substitution C_1 instead of $\frac{\partial T}{\partial x}$, and replacing $T_1 - T_2$ on ΔT in Equation 7:

$$q = \lambda \frac{\partial T}{\partial x}, \tag{8}$$

The ratio of thermal conductivity coefficients of substrates with and without filler in the case of equivalence of external heat fluxes can be estimated by the ratio of the corresponding values of temperature gradients:

$$\lambda_1 \Delta T_1 = \lambda_2 \Delta T_2, \tag{9}$$

Proceeding from the nature of the change of a temperature gradient in the volume of control (a curve 1) and ZnO filled (a curve 2) samples it is possible to conclude that the heat conductivity of both films doesn't differ significantly up to the temperatures about 450 °C.

It is possible to see that the growth rate of temperature gradient for films with a filler slightly exceeds the growth rate of temperature gradient in a control sample. Over 450°C, this tendency doesn't remain.

The dynamics of growth of the temperature gradient in films with filler is reducing in comparison with the control sample. The ZnO filler begins to limit the growth of heat flux through the sample, stabilizing the temperature gradient at the level of 120 - 140 °C. The dispersion of values is about 20 °C.

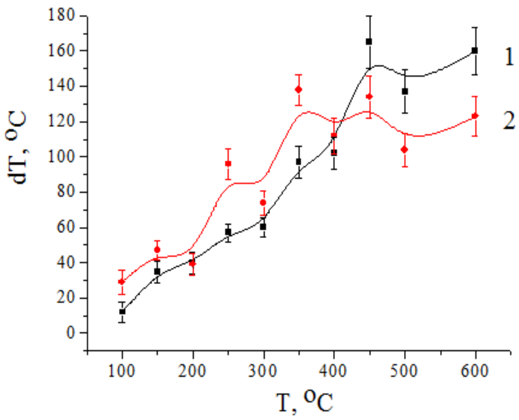

Figure 5. The averaged temperature depends on the film's temperature gradient without ZnO filler (1) and with containing it (2).

The ratios of thermal coefficients $\frac{\lambda_1}{\lambda_2} = \frac{\Delta T_2}{\Delta T_1}$, which characterize the efficiency of ZnO - filler introducing for heat conductivity presented in Table 2. for temperatures above 450°C.

Table 1. Value of temperature gradient in films containing filler ZnO (ΔT_1), in films without filler (ΔT_2), and the numerical ratio of thermal conductivity coefficient ($\frac{\Delta T_2}{\Delta T_1}$).

T, °C	ΔT_1, K	ΔT_2, K	$\Delta T_2 / \Delta T_1$
450	438	407	0,93
500	410	377	0,94
600	422	396	0,94

This ratio averages size about 0.93. Thus, additive significantly changes the constant of heat conductivity of the material of a film in the field of temperatures demanded synthesis architecture of kesterite PEC on it.

Apparently, from Table 2, this ratio averages around 0.93. Thus, the additive ZnO as a filler increases the thermal conductivity of the film material in the specified temperature range. At the same time, the film does not undergo destruction.

5. Conclusions

1. The polyorganosiloxane coverings filled with heat-conducting oxide powder are obtained and their main functional properties are investigated.

2. The conclusion is made that the use of the industrial heat-resistant enamel and powder of not alloyed Zincum oxide in the composition of heat-conducting KPT-8 paste allows us to obtain heat-conducting electrical insulating coverings capable to work in the temperature range demanded synthesis of kesterite (500-600 °C).

3. The mathematical model of thermal processes in a film was carried out. The equation of the process of a heat transfer is received and numerical solutions are found in the form of the ratio of thermal conductivity coefficients for some temperatures in the range of more than 450 ° C.

4. Data of a thermal experiment confirms the possibility of applying for an increase in heat resistance of an electrobarrier coating a dielectric in which there is a thermal activation of processes of diffusion of cationic or ionic sublattices at temperatures that are exceeding the limit of the thermal stability of a natural range of coverings.

6. Patents

Author Contributions: Conceptualization, A.T., O. D., and P.G.; methodology, O.D.; software, O.I., O.P.; validation, O.D., P.G. and A.T.; formal analysis, A.T.; investigation, A.T.; resources, M.B.; data curation, O.D.; writing—original draft preparation, A.T.; supervision, M.B.; project administration, O.D. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare no conflict of interest.

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