RADIATION-INDUCED MODIFICATIONS OF ELECTRICAL PROPERTIES OF VITREOUS DIELECTRIC SiO_2

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The regularities of the radiation-thermal modifications of electrical properties of vitreous dielectric SiO_2 are studied in a broad range of temperatures and ionizing radiation doses. The activation energies are determined, and the non-activation law for the temperature dependence of bulk material electrical conduction is found, whose parameters are different in the low- and high-temperature regions. Experimental results are discussed in the framework of the existing models of charge transport.

Introduction

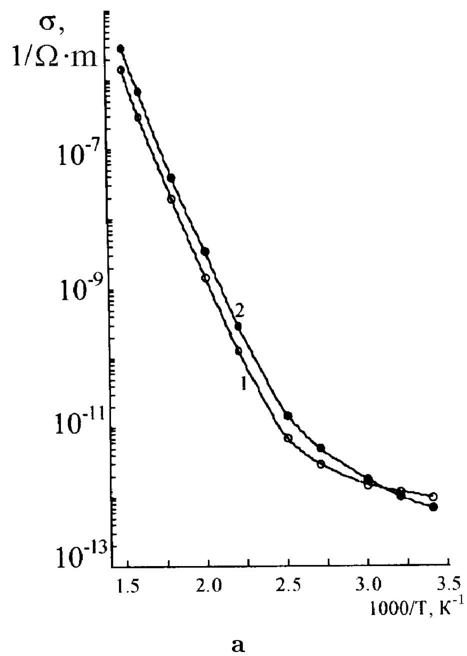
Radiation stability of a number of disordered dielectrics depends on many factors, the most principal of which are the previous history of a material, the state of its structure and defect concentration, its surrounding, temperature, pressure, and radiation dose. Study of the radiation damage of dielectric materials (including ceramic, crystalline, and vitreous materials) was carried out intensively in 1960—70s. Later, the interest in this problem has strongly decreased. However, recently more and more papers devoted to this problem are appearing [1—11]. But a lesser attention is put on the oxygen-containing dielectric materials despite an area of their application continuously broadens. Really, the oxide-containing dielectrics (such as Al_2O_3, SiO_2) are the main components of ceramics as well as a number of optical, laser, radiotechnical, engineering materials and metal-oxide-semiconductor structures [1—4, 6]. They have wide application in various fields of science and technology. Vitreous silica SiO_2 is applied in device engineering, medicine, fiber optics, microelectronics, and nuclear power engineering. It is applied also for the fabrication of radiation protecting shields, airborne radomes, semiconductor substrates, etc. [2, 7, 8]. All this supports the topicality of investigation of radiation stability as well as peculiarities of modification of physical properties of these oxide-containing dielectrics. In particular, this is related to the change of electrical and optical properties under the temperature influence and absorption of ionizing radiation in a wide range of doses.

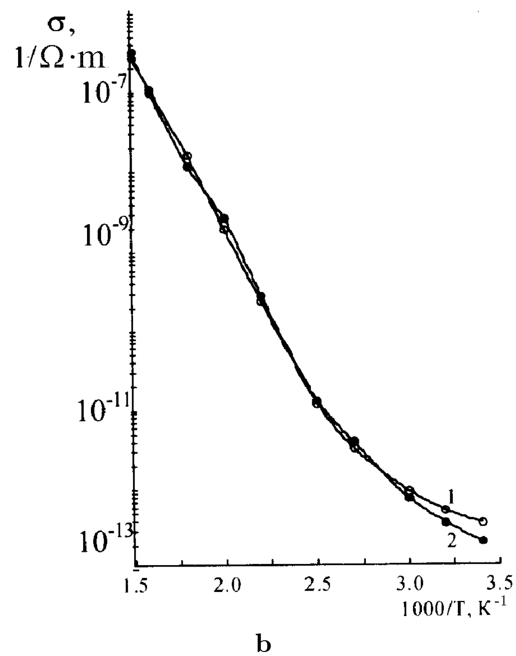
1. Methods and Objects of Investigation

In this paper, the results of the study of ionizing radiation influence on the electrical properties of vitreous dielectrics are presented. The particular attention is paid to the investigation of the effect of different radiation doses both on electrical conduction and dielectric properties of specimens in the temperature range 20—400 °C. The dielectric loss tangent, tg δ, the dielectric permittivity ε, and the electric conduction σ have been measured on the same specimens. Vitreous silica SiO_2 samples of types I and II have been taken as objects for the investigation. The concentration of uncontrolled metal impurities in these samples was about 10^{-2} – 10^{-3} wt. %. The specimens for electrical measurements were 1-2 mm-thick ground wafers of vitreous SiO_2 with deposited non-blocking Ni electrodes. The specimens were packed in a special compact measuring cell, which allowed measuring the required parameters both before and after the irradiation. The measurements were carried out using an IPD-1 device and an EK6-13 teraohmmeter. The specimens were heated by an electrical heater in a measuring cell. The temperature was varied from room one up to 450 °C with precision no worse than ± 0.5 °C. A gamma-setup constructed at the Institute of Nuclear Physics of Uzbekistan Acad. Sci. was used as a Co^{60} ionizing radiation source. The range of doses of the absorbed gamma radiation was $5{\cdot}10^2$—$5{\cdot}10^7$ Gy.

2. Results and Discussion

The results of calculation of the through direct-current conduction σ of type I and II silica glasses, prior to irradiation, are shown in Figure, *a*. It can be seen that the σ values for both types of glass are close in the whole temperature range studied ($T = 20 \div 400$ °C). In Figure, *b*, the temperature dependences of $\sigma(1/T)$ measured on gamma irradiated glasses of both types (absorbed dose $D = 10^4$ Gy), are shown. Comparison of $\sigma_1(1/T)$ and $\sigma_2(1/T)$ values for non-irradiated and irradiated





Temperature dependences of electrical conduction of non-irradiated (a) and irradiated with a dose 10^4 Gy (b) silica glasses: *1* — type I glass, *2* — type II glass

specimens, respectively (Figure,a and b), allows us to conclude that the effect of radiation leads to some decrease of the σ value.

However, the absolute value of the electrical conduction of type II glass is slightly higher than that of type I glass, as can be clearly seen at raising temperature (Figure,a). We suggest that one may explain this by the additional contribution of hydroxyl groups in the type II glass into the electrical conduction [11]. Apparently, the appearance of new radiation-stimulated defects reduces the role of hydroxyl groups in charge carrier transfer. An experiment carried out for the crystalline and vitreous silica has demonstrated that the electrical conduction is almost two orders of magnitude higher for a crystal than that for glass in the temperature range 20—400 °C. Really, the electric conduction of glass is expected lower than that of a crystal at least because of the charge carrier lifetime in glass is considerably smaller due to the disordered structure.

The treatment of the graphs $\sigma(1/T)$ for gamma irradiated glasses has shown that these graphs can be described by a formula taken from [1], similar to the case of irradiated ceramics. We calculated the constant values (a, A, B) in this formula and the activation energy E_a of the conduction process. In general, the calculated values are typical of vitreous dielectrics. However, the values of some constants are closer to those for crystals (A, B) and ceramics (a, E). The values of activation energy in the high-temperature region (i.e. in the region with steeper $\sigma(1/T)$ dependence) have been obtained as follows: $E_a = 1.02$ eV and $E_a = 1.00$ eV for non-irradiated and irradiated specimens, respectively. The calculated results allow us to conclude that the character of electrical conduction of radiation-treated vitreous dielectrics has not changed significantly.

A study of the influence of higher gamma radiation doses (constant radiation power $P_\gamma = 11$ Gy/s) on the electrical conduction of vitreous dielectrics is of particular interest. The results of measurements of σ for type II glass at an approximately constant temperature, varying the absorbed dose from 10^3 to 10^6 Gy, are shown in Table 1.

A characteristic feature of the dose dependence of the specimens studied, is a $\sigma(D)$ non-linearity. A critical point is found on it at $D = 1{\cdot}10^5$ Gy. A gradual decrease

T a b l e 1. Radiation-thermal dependence of the electrical conduction of type II glass for several temperatures, $\Omega^{-1}{\cdot}m^{-1}$

T °C	D, Gy			
	10^3	10^4	10^5	10^6
50	$7.8{\cdot}10^{-13}$	$5.2{\cdot}10^{-13}$	$3.9{\cdot}10^{-13}$	$7.8{\cdot}10^{-13}$
100	$3.9{\cdot}10^{-12}$	$1.3{\cdot}10^{-12}$	$7.8{\cdot}10^{-13}$	$1.3{\cdot}10^{-12}$
150	$2.0{\cdot}10^{-11}$	$1.7{\cdot}10^{-11}$	$1.6{\cdot}10^{-12}$	$9.1{\cdot}10^{-12}$

of ionization effectiveness apparently occurs during the initial period of irradiation. Then, at the irradiation dose increase, the ionization effectiveness also increases. It can be seen from Table 1 that such a radiation kinetics of electrical conduction takes place at $T \leq 150$ °C. Therefore, a "small-dose effect" is observed under the experimental conditions described, when the electrical conduction of a specimen decreases with the radiation dose increase.

It is known [1] that the gamma-quanta induced ionization in a dielectric results in the increase of an induced electrical conduction, according to the formula:

$$\sigma_p = en\mu, \qquad (1)$$

where σ_p is the conduction component due to the ionizing radiation, e is the elementary charge, n is the concentration of free charge carriers, and μ is the charge carrier mobility which depends on the structure, dose, and temperature of irradiation. In the region of radiation doses under consideration, gamma-quanta create a series of color centers in silica glass, e.g. as a result of capture of radiation induced electrons by atoms [12—14]. In this case, a radiation-stimulated defect diffusion takes place, which influences the parameters n and μ in formula (1). All this can be the main reason for the value of σ to decrease in vitreous dielectrics with the dose increase up to 10^5 Gy, taking additionally into account that gamma radiation modifies the spectrum of pre-irradiation and radiation-induced defects.

We carried out the investigations of a change of the dielectric loss tangent tg δ and relative dielectric permittivity ε which was calculated by the formula [15]

$$\varepsilon = (d/\varepsilon_0 S)C_x, \qquad (2)$$

where d is the specimen thickness, ε_0 is the electrical constant, and C_x is the experimentally measured specimen capacity. The measurements have been carried out prior to and after the gamma irradiation in the frequency range 0.3—30 kHz, varying the temperature from 20 to 400 °C. The results of measurements of dielectric parameters for type I glass are shown in Table 2. Analogous results have been also obtained for type II glasses.

It can be seen from this Table that the temperature dependence of the loss tangent has a complicated nature. At low temperatures and frequency $f = 300$ Hz, the tg δ value decreases somewhat, when the specimens are heated up to 200 °C. Then, at $T > 200$ °C, the tg δ value sharply increases, i.e. the slope angle of a temperature dependence changes here and preserves its value up to 400 °C. The decrease of losses (especially at $T < 200$ °C) can be related to the concentration decrease of elements, which are polarized, or to the decrease of their mobility under electron (hole) localization in shallow traps created by radiation. The increase of losses at $T > 200$ °C is apparently related to the increase of the role of ion thermal polarization processes under radiation-thermal material treatment. The growth of the alternating current frequency up to 1000 Hz leads to the decrease of tg δ both in irradiated and not irradiated specimens in the whole temperature range (Table 2). It is known from theory [1] that the increase of the alternating current frequency leads to a decrease of losses (tg $\delta \sim 1/f$). As can be seen, the ionizing radiation does not break this regularity and preserves an inflection point of tg $\delta(T)$ typical of non-irradiated glass.

The appearance of the inflection point on the temperature dependence of tg δ of the specimens under study (Table 2) is apparently determined by an increase of the contribution of ionic thermal polarization processes, i.e. the role of ionic component increases with the temperature raise. An analogous inflection is observed on the temperature dependence of glass electrical conduction (Fig. 1). Such a form of the dependence of tg δ(T) for electroceramic is explained in [1] by an increase of the ionic component of conduction. We suppose that this explanation is also applicable for vitreous dielectrics. The inflection preservation after the irradiation in this case supports the prevailing role of temperature stimulated processes. The increase of losses at $T > 200$ °C is apparently due to the increase of the

T a b l e 2. Dependence of the tg δ and ε on the frequency and the temperature for type II glass specimens

T °C	$f = 300$ Hz				$f = 1000$ Hz			
	tg δ		ε		tg δ		ε	
	non-irradiated	irradiated	non-irradiated	irradiated	non-irradiated	irradiated	non-irradiated	irradiated
50	$3.8 \cdot 10^{-3}$	$6.5 \cdot 10^{-4}$	4.98	5.05	$1.8 \cdot 10^{-3}$	$5.0 \cdot 10^{-4}$	4.98	5.05
100	$3.5 \cdot 10^{-3}$	$5.0 \cdot 10^{-4}$	4.98	4.99	$2.2 \cdot 10^{-3}$	$2.0 \cdot 10^{-3}$	4.98	4.98
200	$2.0 \cdot 10^{-3}$	$3.1 \cdot 10^{-3}$	4.98	4.99	$1.2 \cdot 10^{-3}$	$3.5 \cdot 10^{-3}$	4.98	4.99
300	$8.2 \cdot 10^{-2}$	$3.5 \cdot 10^{-2}$	5.03	5.00	$2.0 \cdot 10^{-2}$	$1.7 \cdot 10^{-2}$	4.98	4.99
400	$6.4 \cdot 10^{-1}$	$4.8 \cdot 10^{-1}$	5.45	5.07	$2.5 \cdot 10^{-1}$	$1.6 \cdot 10^{-1}$	5.28	5.06

concentration of particles, which takes part in polarization processes stimulated by temperature and ionizing radiation.

It is found that the dielectric permittivity of a non-irradiated specimen is stable at a frequency of 300 Hz, when a temperature is raised up to 200 °C (Table 2). However, the further heating leads to the increase of ε as well as to the change of its temperature dependence slope, which can be seen up to 400 °C. The influence of radiation at a dose $D = 10^4$ Gy leads to a slight increase of the dielectric permittivity of specimens. In general case, however, the form of the temperature dependence preserves, although the change of ε below 400 °C is far smaller. Therefore, in the temperature range $T > 200$ °C, the effect of radiation is a decrease of the $\varepsilon(T)$ dependence. Raising the frequency up to 1000 Hz for the initial specimen leads only to the decrease of ε at 400 °C (Table 2).

From the analysis of the results obtained, we may conclude that ionizing radiation leads to a change of dielectric characteristics of type I and II glasses (Table 2). These results contradict the results obtained in [16], where no change of dielectric parameters has been observed in fused silica after gamma irradiation. Such a difference is possibly related to the usage of silica glass specimens with different histories, compositions as well as to the application of different kinds of equipment and measuring technique.

In [9], we have investigated the effect of gamma radiation on the optical spectra of different SiO_2 specimens in ultraviolet and visible spectral range. In particular, the dose dependence of the accumulation of color centers at 540 nm has been determined for type I and II glasses. The proportional growth of the concentration of these centers with the absorbed dose increase from $1 \cdot 10^2$ to $5 \cdot 10^5$ Gy was found out, as well as the following decrease of the color center generation with the saturation of $Y(D)$ curves. Then, the kinetics of thermal fading of the coloring induced in specimens has been determined. According to the data obtained, the dependence $Y_{\rm ann}/Y_{\rm irrad}(T)$ is stable up to 250 °C and then (up to 450 °C) intensively decreases up to the complete fading of visible color.

After the comparison of the obtained radiation-thermal dependences of optical (absorption spectra in the visible region) and electrical (electrical conduction) characteristics, a conclusion on the antibate behavior of the kinetics under consideration was drawn, since the region of a radiation induced decrease of the electrical parameter is a reflection of the region of respective optical density growth at 540 nm.

It is known [9, 12, 13] that the center absorbing at 540 nm is of electronic nature. It is an electron captured by a bridge oxygen vacancy in neighborhood with an Al^{3+} ion. This supports the above-presented assumption of a decrease of glass conduction with the growth of irradiation dose. A considerable amount of electrons appears on the action of ionizing radiation on silica glasses. These electrons are captured by traps, which leads to the formation and accumulation of color centers with the irradiation progress (e.g., at 540 nm), on the one hand, and to a decrease of the free charge carrier concentration (hence, glass electrical conduction), on the other hand. Then, at higher doses, the relation of the carrier recombination and generation processes can change, or the stimulated diffusion coefficient of electrons and ions and their mobility can increase, which can result in the radiation conduction growth by formula (1). This is possible when the curves $Y(D)$ of color center generation come to a saturation, and the curves $\sigma(T)$ pass through a turning point. All the written above supports that electrons are charge carriers in the disordered SiO_2 material.

In addition, the SiO_2 electrical conduction decreases, i.e. the stage of radiation annealing appears again in $\sigma(T)$ under a further raise of the absorbed dose up to the values of the order of $5 \cdot 10^7$ Gy and more. The parameter value comparing to that at the initial stage significantly decreases in this case (almost by two orders of magnitude), which correlates to a certain extent with measured absorption spectra (since a tendency of optical density decrease at 540 nm appears). Such an electrical conduction decrease of high-dose irradiated specimens is interesting, since it shows a possibility of SiO_2 application, e.g., for the fabrication of protecting shells or radomes under space conditions.

The physical properties of disordered materials have some peculiarities comparing to those of respective single-crystalline substances. For electrical properties, this is true for the charge transfer process, when the activation energy of conduction decreases fluently with temperature. In this case, one may draw the tangents on a temperature dependence, the slopes of which accord to different values of activation energy. Conventionally, the curve $\sigma(T)$ is described by a sum of several exponents, which accord to different mechanisms of conduction. As was noted previously, the results obtained for our materials can be described at the first approximation by formula (1), which includes an exponent and the function $T^{3/2}$. Recently, the opinion is expressed [17] that these curves can be described not by multiple exponents but by a single law, as well as about the role of polaron effects for some disordered materials. This has motivated us to carry out a more detailed analysis and a treatment of the curves $\sigma(T)$ obtained in this work for structurally inhomogeneous dielectric SiO_2 (Figure).

It turn out that the conduction of materials in the low temperature region (20—130 °C) can be well fitted by a linear dependence in logarithmic coordinates $\sigma - T$. This means that the dependence looked for vitreous silica obeys a power law:

$$\sigma = \mathrm{const} \cdot T^n. \quad (3)$$

According to [17], the curves $\sigma(T)$ for amorphous boron and borides can be described by a power law, i.e. they have polaron conduction. The possibility of polaron formation in non-crystalline materials has been analyzed by a number of authors [18]. It has been noted that the probability of this process increases significantly in disordered systems, comparing to crystalline systems. The results of these investigations for SiO_2 apparently agree with this opinion. It is assumed that a charge carrier stays near a lattice point for some time, which leads to a neighboring atom displacement and the formation of a potential well which captures this carrier. The well depths can be various.

The exponent in formula (3) usually characterizes a number of photons taking part in the transfer process. According to the results of approximation of the temperature dependence of σ for both initial and irradiated glass specimens, in the temperature region shown above (Figure), as well as according to the obtained values of n, six phonons are enough for a carrier hopping in the first case, and eight phonons in the second case. It can be seen that irradiation has slightly increased the parameter n in formula (3). Therefore, one may conclude that the SiO_2 conduction at low temperatures obeys the power law, which is related to multiphonon carrier hoppings.

It is found that a power dependence of $\sigma(T)$ turns into other non-activation dependence at raising temperature from about 130 °C up to 400 °C. Processing of the obtained results has shown that, for glass, the dependence corresponds to the so-called inverse Arrhenius law in the region of elevated temperatures:

$$\sigma = \sigma_0 \exp(T/\alpha^{-1}T_0), \quad (4)$$

where α^{-1} and T_0 are parameters. Hence, law (4) is valid at higher temperatures, $T > 130$ °C in our case. According to the concept developed in [17], the charge transfer in a conductivity of the type (4) is realized by a one-phonon electron hopping process from one state into another. The calculations made for SiO_2 according to formula (4), have resulted in the following parameters of this formula: $\alpha^{-1}T_0 = 25$ K for non-irradiated specimens, and 26 K for irradiated specimens. It can be seen that irradiation has not changed a numerical value of this parameter in formula (4). Usually, this parameter characterizes the effective depth of a potential well. The $\alpha^{-1}T_0$ values obtained for vitreous silica are not large and accord to small well depths, several meV. Therefore, one may assert from the stated above that the gamma radiation has not led to a change of a potential well depth. At temperatures higher than this parameter, the material conduction still obeys to the inverse Arrhenius law.

It is known that the material disorder can be of different character. For vitreous SiO_2, these are glass structure imperfections (Si—O—Si bond lengths and angles distortions), regions with increased concentration of grown-up defects, impurities, microinclusions (small-size crystallites, pores), etc. Such a diversity of structural defects leads to a heterogeneity of a current in the material, since there are regions which participate or do not participate in the process under consideration. The main reason for this is the presence of a disorder in glass on a scale of 10^{-7} cm. This disorder leads to exponentially large spatial fluctuations of charge carrier mobility $\mu(r)$. It is assumed that only carriers from a narrow energy interval near a passing level, which accords to the formation of a critical conductive cluster, play a dominating role in charge carrier transport in disordered materials. Possibly, the carriers from a potential well are excited at the passing level and drift there, when the temperature of our material is raised ($T > T_0$). This means that in a wide temperature range (130—400 °C), the dominating mechanism of charge transfer is the carrier transport at the passing level of a given cluster, and that the conduction as a function of temperature agrees with (4).

Conclusion

The characteristic features of the temperature dependence of electrical conduction before and after the gamma irradiation have been found for the materials studied. The values of the activation energy of direct-current conduction have been determined as well as their preservation after the irradiation has been demonstrated. The improvement of electrical properties of dielectrics irradiated by large-dose gamma radiation has been shown which points to the prospects of application of such dielectrics in radiation fields. The

peculiarities of electrical conduction dependence upon dose have been found, as well as the appearance of a minimum of the function $\sigma(D)$ at a dose about 10^7 rad. The dose dependences of optical and electrical parameters have been compared and the nature of charge carriers has been discussed. The change of dielectric parameters tg δ and ε upon T and f of non-irradiated and irradiated materials has been found out. The non-activation law of the temperature dependence of material conduction has been found, the analytical expression of which depends on the temperature range. The numerical values of parameters of this law have been calculated. The obtained results have been analyzed in the framework of the known models of charge transfer.

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РАДІАЦІЙНІ ЗМІНИ ЕЛЕКТРИЧНИХ ВЛАСТИВОСТЕЙ СКЛОВИДНОГО ДІЕЛЕКТРИКА SiO_2

I.А. Абдукадирова

Р е з ю м е

Досліджено закономірності радіаційно-термічних змін електричних властивостей скловидного діелектрика SiO_2 в широкому інтервалі температур і доз іонізуючого випромінювання. Визначено енергії активації. Для температурної залежності об'ємної електропровідності матеріалу виявлено неактиваційний закон, параметри якого різні для області низьких та високих температур. Експериментальні результати проаналізовано в рамках існуючих моделей переносу заряду.