

The Influence of the Dispersion of Boron Silicate on the Migration of Non-Equilibrium Charge Carriers Generated by Effect of an Electric Discharge

A.M. HASANOV
*Radiation Research Sector,
Academy of Sciences, H. Javid av., 31 a,
370143 Baku - AZERBAIJAN*

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Abstract

ESR was used in an investigation of the influence of Boron Silicate dispersion on the accumulation of paramagnetic centers (PC). It was observed that the rate of accumulation of PC increase by increasing of the grain size (r). At $r < 0.08$ mm the electrons (F^+ -centers) are localized on the surface and with increasing grain size up to $0.08 < r < 0.22$ mm charge stratification takes place, the electrons are distributed in near-surface layer and the holes (V -centers) are localized in the bulk of the insulator. It was established that the transport of non-equilibrium charge carriers (NCC) from the bulk to the surface of Boron Silicate was due to a drift from the depth ($d \sim 10\mu m$) to a bulk-charge field generated by an electric discharge. The value of the surface field $E_s \sim 10^5 V/cm$ is determined by experimental results of the data. The kinetics of the isothermal annealing (300 K) are used to establish the influence of the surface field on the annihilation of NCC in the "dead" layer of separated charges.

1. Introduction

In heterogeneous systems the discharge [1, 2] and radiation [3-8] stimulated processes and their conclusion are mainly determined by the generation and the transport of free and localized NCC and excited states [4, 9] from the bulk to the surface of solids. It was shown [2-6] that the migration of the electrons, holes and their excited states to the dielectric surface is due to their drift in the near-surface layer of the space-charge formed by irradiation. The surface field suppresses the bulk recombination processes and causes the changes of the mechanism of formation of localized and excited states. The presence

of the surface field is the main factor for the transfer of NCC and for the change of nature of localized states as well as for the explaining of mechanism of the defect formation at an interface between phases in the same substance. This can be used practically for the designing of radiation and plasma technologies.

Therefore the influence of B_2O_3/SiO_2 surface on the nature and the generation rate of localized charges at 77 K and on their destruction by isothermal annealing at room temperature in dependence on the Boron Silicate dispersion has been investigated.

2. Experimental

The B_2O_3/SiO_2 powders synthesized by the method described in [11] were used. 97 % of SiO_2 and 3 % of B_2O_3 formed the mass content of Boron Silicate. The separation of powders into fractions of different sizes ($0.03 \leq r \leq 0.22mm$) was carried out by sieving. For defining the average size fraction the MMP-4 microscope method was used. To obtain the appreciable difference between measured values, including the concentrations of localized charges, the following fraction sizes were chosen: $r = 0.03, 0.05, 0.08, 0.1, 0.15, 0.2, 0.22mm$. At first, each fraction of B_2O_3/SiO_2 was separately placed in a 16 mm diameter glass tube having quartz and molibden sections. To the molibden part narrow discharge molibden ampoules (diameter 4 mm) were approximately perpendicular soldered. After thermovacuum treatment ($T \simeq 873K$, $P \simeq 10^{-2}Pa$) both in air and oxygen flows for 48 hours in the quartz section of the tube the samples were introduced into discharge ampoules without disturbing the vacuum. The discharge ampoule was additionally heated to 650 K. After that they were unsoldered at $\simeq 1.3Pa$ air pressure and the samples were exposed to electric discharge (ED). The discharge ampoule was a cylinder capacitor a small part of which was filled with powder of Boron Silicate up to 8 mm. The inner electrode of discharge ampoule manufactured from platinum wire with diameter of 3 mm was placed in the center of ampoule with sample and connected to high voltage source at (50 Hz). The external electrode made from aluminium foil was grounded. The discharge ampoule was introduced in a vessel made from dielectric and filled with liquid nitrogen. The barrier ED was carried with a constant alternating field ($E \approx 3 \cdot 10^6 V/m$). After the exposure the ampoules with samples were placed into a finger dewar for $0.5 \div 1s$ and then installed in an ESR resanotar.

ESR spectrum was recorded using an RE-1306 at wave length of 3,2 cm at 77 K and 300 K. The concentration of PC and the g-factors were determined by the method described in [12] for the singlet structure; and for the presence of hyperfine structure (HFS), the method described in [13] was used. In both cases, to increase the reliability of the results, additional analysis of HFS was carried out using an SE/X 2544 ESR-spectrometer (Poland, supplied with a computer "Micropan"). The comparison standards were radicals of silicon monoxide (SiO) and Mg^{2+} -ions in the MgO lattice, respectively.

3. Results

Under identical experimental conditions for the different fractions of Boron Silicate discharged in air at 77 K, the ESP spectrum and the rate of accumulation of localized charges for the same substances are different (Figure 1). It was established that for the grain sizes $r > 0.08mm$ of B_2O_3/SiO_2 the spectrum is a single symmetrical singlet with parameters $g_{F^+} = 2.001$, $\Delta B_{F^+} \sim 0.4mT$. With the admission of NO and O_2 , the signal intensity increases and is easily saturated by UNF power. The singlet refers to the trapped electron, i.e. $V^{2+} + e^- \rightarrow F^+$ (Figure 1a). Increasing the grain size of B_2O_3/SiO_2 to $0.08 \leq r \leq 0.22mm$ leads to the appearance of a new multicomponent pattern which has a sharply defined HFS from the $^{11}B(I = 3/2)$ nucleus with the parameters $g_1 = 2.002$, $g_2 = 2.011$, $g_3 = 2.039$ and A-tensor components $A_1 = 1.2mT$, $A_2 = 1.4mT$ (Figure 1b).

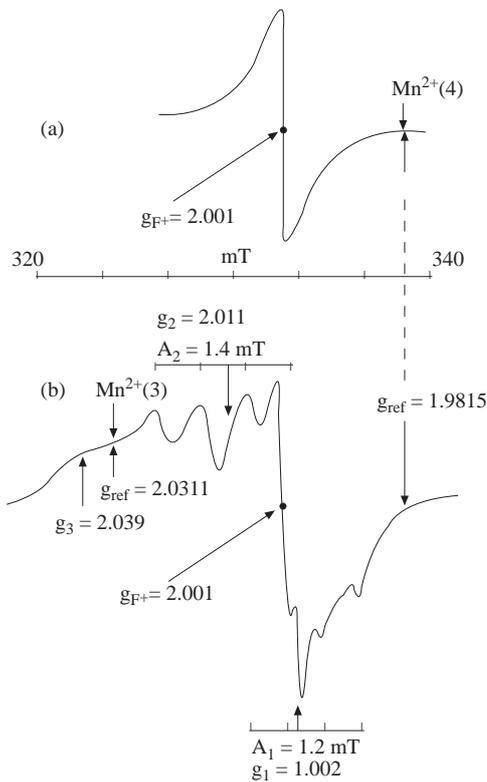


Figure 1. ESP spectra of B_2O_3/SiO_2 exposed to the action ($t = 30$ min) electric discharge at 77 K. $E = 3 \cdot 10^6 V/m$; $P = 1.33Pa$; $r = 0.03mm$ (a) $r = 0.08mm$ (b) and $t = 30$ min.

This pattern refers to the hole centers. It is impossible to determined the constant A_3 because the HFS is not found in the region of low magnetic fields for the g_3 .

The analyses of spectroscopic data of multicomponent pattern shows that the interaction of B_2O_3/SiO_2 -surface with H_2, H_2O and CO causes the change of intensity with additional lines. Moreover, the thermal destruction of localized states demonstrates that these lines belong the hole centers of different types: the less stable structural defects and the thermal stable holes trapped by Boron atoms and localized at "non-bridge" oxygen atoms. The study of the action of different donor - (H_2, H_2O, CO) and acceptor (NO, O_2) gases on the concentration of defects in B_2O_3/SiO_2 before and after ED exposure in the air shows that O_2 and NO have a strong influence on the formation of defects.

With an increase of the grain size to 0.2 mm the rate of accumulation of PC (W_{pc}) increases monotonically, depending on sizes, i.e. $W_{pc} \sim f(r)$ and for $r > 0.2mm$ it reaches saturation and becomes stabilized (Figure 2). In the case of F_+ -centers the dependence $W_{F_+} \sim f(r)$ is rather weak in comparison with that of holes, which are characterized by their great thermostability. The analysis of kinetics of isothermal annealing of the defects in B_2O_3/SiO_2 for two extreme granula sizes (0.03 and 0.02 mm) at room temperature and under continuous influence of photons of visible light (the photon energy was $\sim 1.6 \div 3.1eV$) shows the surface influence on the processes of destruction (or migration) of localized charges (Figure 3). The rate of the annealing of defects is two times greater for granule size $r = 0.03mm$ than that of samples with granule size $r = 0.2mm$ and the photons of visible light accerelate mainly the destruction of the hole centers.

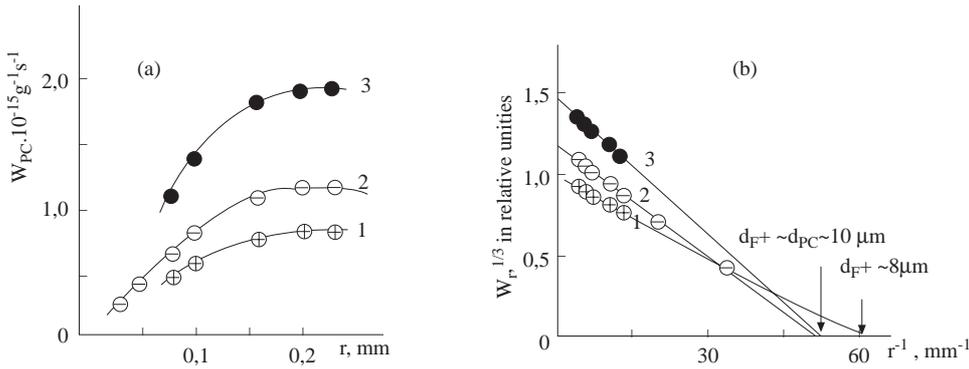


Figure 2. Dependence of accumulation rates of hole V^- (1), electron F^+ (2) and sum paramagnetic centers (3) in B_2O_3/SiO_2 on grain sizes (a). Changes of relative rates $W_r^{1/3}$ versus inverse value of granule size (b), where $W_r = \frac{W_{pc}(r)}{W_0}$ at $T = 77K; E/P = 2.25 \cdot 10^6 V/mPa$.

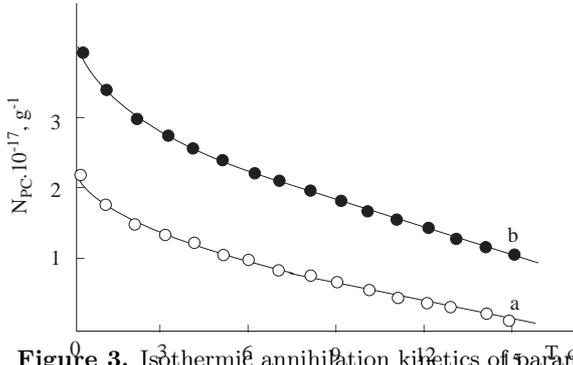


Figure 3. Isothermic annihilation kinetics of paramagnetics centers under the action of visible light photons at $T = 300K$; $E/P = 2.25 \cdot 10^6 V/mPa$; $r = 0.03mm$ (a) and $r = 0.22mm$ (b).

4. Discussion

Determination of the charge state of the surface using physical or chemical methods is necessary to define the change of characteristics the formation rate and the destruction of the NCC in Boron Silicate.

To solve the problem, the chemical approach was chosen. The results of interaction of B_2O_3/SiO_2 surface with different gases of donor and acceptor type (H_2, H_2O, O_2, CO, NO) after an exposure to ED show that the surface of the Boron Silicate is charged negatively. The appearance of the singlet line in ESR spectrum for granule size $r < 0.08mm$ referring to the electrons trapped by the surface vacancies of oxygen of dielectric [8-11] can confirm the above conclusion. On that base, the absence of ESR-signal from the hole center can be explained. In the process of exposure of B_2O_3/SiO_2 to an ED the separation of electron-hole pair occurs under the influence of two fields:

- 1) The electrostatic field of interaction between two charges connected genetically, i.e. of interaction between electrons and holes characterized by the Onsager surface action (Onsager radius $r_c = e^2/4\pi\epsilon_0\epsilon KT$);
- 2) The surface field due to localization of some electrons in the near-surface traps.

The holes from separated pairs have life times too short for localization on the cation vacancies or, practically, do not reach to them due to charge trajectory bending by the surface field lines. In this case, the drift rate is added to the thermal movement of holes and, colliding with free and localized electrons (or F^+, F -centers), recombine and disappear. Therefore the ESR signals from the hole center are not observed at the small grain size of Boron Silicate. But it does not mean that the hole localization in B_2O_3/SiO_2 does not take place. In reality the holes are localized and the number of these holes is much less than the minimal value observed by ESR spectrometry.

However, for grain sizes $r > 0.08mm$ the observed picture becomes complicated. The full ESR spectrum of B_2O_3/SiO_2 include the spectrum from the hole center [8, 9] with clearly observed HFS from ^{11}B nucleus [9-11]. The intensity of the hole center lines at the interaction of surface V^- -centers with donors molecules is almost not changed. In the case of the interaction their with acceptors the results in the same effect as in the case of interaction with electron centers.

Hence we conclude that the separation of the charges results in their stratification, i.e. electrons are localized in the near-surface layer forming the F^+ electron centers, and the holes at the V^- hole centers in the "bulk" of the dielectric. Between these charges there is a region called the "dead" layer [2, 3] of electric fields, where the migration and recombination of charges take place. The existence of the surface field and of the recombination layer is the cause of the changes of the nature and of the rate of accumulation of localized NCC in B_2O_3/SiO_2 which were generated under the effect of ED. Analogous to the results of [2, 3], when imagining the powder grain as a sphere, in the first approximation for the rate of accumulation of localized NCC an identical expression is obtained:

$$W_{pc}(r) = W_0 \left(1 - \frac{d}{R}\right)^3 = W_0 \left(1 - \frac{2d}{r}\right)^3, \quad (1)$$

where W_{pc} and W_0 are the rates of accumulation of localized NCC in the presence and the absence of the near-surface "dead layer", d is the thickness of the "dead layer", $r = 2R$ is the parameter representing the linear size of a grain which is equal to the size of the sieves cell.

Two limiting cases in the dependence of (W_{pc} on) grain size can be considered from expression (1):

- 1) $r \rightarrow d$, then from (1) $W_{pc}(r) \rightarrow 0$,
- 2) $r \gg d$, then $W_{pc}(r) = W_0$.

Hence if the particles are large ($r \gg d$) the contribution of the near-surface layer during the accumulation of localized charges is small and it can be neglected. The real defect structure in the solid dielectrics are due the presence of the near-surface layer of localized charges in them. Therefore the defect structure processes and also the accumulation rate of localized NCC can't endlessly increase, and stabilizes near the maximum values which are observed by experiment at $r > 0.2mm$ (Figure 2). However with the reduction of grain size up to $r > d$ in Boron Silicate the rate of accumulation $W_{pc}(r)$ reduces. At $r = d$, a very low value of W_{pc} or absence of rate of accumulation must probably be observed due the action of the surface field on the bulk recombination of different NCC in B_2O_3/SiO_2 .

The value of d was estimated in order to confirm the properties of given effect and to detect the influence of its action. The experimental curves (Figure 2) are plotted employing the coordinates $(W_r^{1/3}, r^{-1})$, where $W_r = \frac{W_{pc}(r)}{W_0}$. The obtained dependences

are straight lines from which the value of d for electron, hole and total PC's can be easily estimated (Figure 2b). For constant $E/P \sim 2.25 \cdot 10^6 V/m Pa$ we have $d_{F+} \sim 8\mu m$, $d_{v-} \sim 10\mu m$ and $d_{pc} \sim 10\mu m$, respectively.

The experimental values of d enable to estimate the constant W_0 via equation (1) at $W_0 \sim 1.2 \cdot 10^{15} g^{-1} s^{-1}$. Moreover, we determine the value of surface field E_s by the expression:

$$d = \mu E_s \tau, \quad (2)$$

where μ is the drift mobility of the charges and τ is their total life time in the band.

From [14, 15] it is known that for the wide band oxide dielectrics with ionic bonds μ is approximately $10 \div 40 cm^2/Vs$ and τ is limited by $10^{-8} \div 10^{-10} s$ i.e. the NCC drift to the surface in time which is less than the duration of existing factor and is $10^{-6} - 10^{-8} s$ for the barrier ED [16, 17]. Substituting these data into equation (2) we obtain $E_s \sim 10^5 V/cm$ which is a rather reasonable value for the field providing a drift of the charges to the Boron Silicate surface.

Then it is necessary to refine the change of the effect of the surface field in dependence on dispersion of the sample. There are two assumptions:

- 1) The value of field depends disproportionally on the inverse values of the granule sizes, i.e. $E_s \sim f(r^{-1})$;
- 2) The value of the surface field remains constant regardless of granule sizes, i.e. $E_s \sim f(r^{-1}) = \text{constant}$ while the ratio of "passive" and recombination volumes is only changed.

Indirect answers to these questions can be obtained in kinetics by the investigations on isothermal annihilation of PC at 300 K under the influence of photons of visible light ($\epsilon_{PH} \sim 1.6 \div 3.1 eV$) for two extreme granule sizes (0.03 and 0.02 mm) (Figure 3). The kinetics of annealing of PC is initially (during $\tau \sim 2 - 3$ days) near exponential and then becomes purely a straight line.

In the initial region kinetics the rate of annealing of defects, its significant difference for both fractions of B_2O_3/SiO_2 , allows to maintain the influence of near-surface layer on NCC migration to the surface. The linear nature of the dependence $N_{pc} \sim f(t)$ in the following region of kinetics confirms the diffusion destruction of PC.

It must be noticed that the existence of exponential character of the initial region of kinetics for two extreme granule sizes (0.03 and 0.22 mm) and the difference of the rate of destruction and that of accumulation of NCC in diffusion region allow probably to confirm the first assumption.

If the second assumption is true, it is necessary to maintain the parallelism of curves of the PC destruction in all regions of the relation $N_{pc} \sim f(t)$ that is not observed by the experiments. However it was found out that for small grain sizes of Boron Silicate (-0.03 mm) the annealing rate of the centers becomes 2 times greater in respect to that of the (0.22 mm) fraction. The influence of visible light accelerates the rate of destruction

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of the hole centers due to the sufficiency of energy of holes leaving the cation vacancies. Moreover, for grain size $r < 0.03mm$ the role of the surface field is significant and the effect of it suppresses completely the increase of the number of localized charges [4, 18] due to the increase of the active surface of Boron Silicate. Therefore, it was found from the obtained values of d and E_s that the depth of migration of electrons and holes from the bulk to the surface of B_2O_3/SiO_2 and the sphere of action of electric field are connected with one and the same characteristic property of the dielectric, the surface charge state of Boron Silicate occurring by the exposure of electric discharge.

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