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Influence of Medium on Generation of Localized Charges in BeO by the Exposure of the Electrical Discharge in Air and Oxygen

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Abstract

The EPR-method is used to investigate the regularity of the formation of paramagnetic F^+- and V^- centers (PC) in BeO which are generated by barrier electrical discharge (ED) in air and oxygen under reduced pressure. It was determined that, at different powers of discharge or parameters E/P, the maximums of kinetic curves of PC- accumulation in oxygen in comparison with air plasma forming medium are changed with resspect to both their value and position, depending on the interaction of oxygen atoms and ions $O, O^+, O^-, O_2^+, O_2^-, \ldots)$ with BeO surface. These exposures resulted in decreasing rate of generation of F^+-and V^- centers in oxygen plasma in comparison with discharge in air (at $t > t\max$) and the difference of their concentration in the stationary region ($t \to \infty$) of PC-acumulation curves for the same E/P.

1. Introduction

The physical state of the surface or near-surface layer of BeO under the action of penetrating radiation [1-4] and ED [5-7] is mainly determined by the localization of non-equilibrium charge carries (NCC) both on the surface and in the dielectric bulk. The result of the effective interaction of neutral and charged particles from a plasma forming medium with the contact surface of dielectric is the generation of active local surface states [8-11], which further contribute both to chemical transformation and to physical-chemical dissipation of energy of the extermal exposure factors on the surface of dielectric. Moreover, the processes of generation and stabilization of NCC in solid dielectic and particularly in BeO, under the influence of radiation and ED, mainly depend not only on the state of BeO surface but also on the donor-acceptor features of surrounding gaseous

medium [10,14,15]. The distinctive features of this process are also revealed in some gaseous media with similar physical-chemical properties, such as air and oxygen.

Therefore, using the EPR-method, we investigated the influence of air and oxygen, with variation of their pressures, on the processes of localized charges generation in BeO by ED exposure. This investigation has vital importance for different practical aims, on of which relates to the eloboration of physical and chemical processes in plasma reactors.

2. Experimental

Powder BeO samples were marked "for luminophors" with $S_d \sim 60m^2/g$ and 10^{-4}%-impurity. After being thermal vacuum treated ($T = 873K, P = 10^{-2}Pa$) in a quartz pipe (consisting of quartz and molybdenum sections) for 6 days in oxgen ther sampres were placed into narrow 4,2 mm diameter discharge ampoules previously soldered to the molybdenum section of the pipe. After additional heating at 727 K and at different pressures of air and oxygen in the range of from 1,3 to $3 \cdot 10^4 Pa$ they were unsoldered. Each discharge ampoule was made narrow above the level of the BeO powder in order that the particles did not rise upward during the discharge.

The discharge ampoule is a cylindircal capacitor the samll part of which is filled with BeO powder up to ~ 8 mm. The internal electrode mode from $\sim 0.3mm$ platinum wire was placed in the centre of the ampoule and connected to a high voltage source (ÇII-70M with f=50Hz); the external electrode made from aluminium foil was grounded. Then the ampoules were placed into a dielectric vessel filled with liquid nitrogen and at the constant value of applied alternating field (E=$2.5 \cdot 10^6$ V/m) the ED barrier was created out.

After the exposure, the ampoules with samples were placed into a finger dewar filled with liquid nitrogen and then into a EPR resonator.

EPR spectra were registered using the radiospectrometer RE-1306 with 3,2 cm wave length and temperature 77 K. PC-concentration and g-factors were determined by the method described in [5,6]. The radicals of silicon monoxide ($Si\dot{O}$) and Mn^{2+} ions in the MgO-latice were used as a standard.

3. Experimental Results

EPR spectra of BeO discharged at different pressures of oxygen or air 0plasma and registered at 77 K are doublets consisting of wide and a narrow lines which are identical to these of the gamma-irradieted samples of the same powders (Figure 1.). The spectroscopical data (g-factor, line wide), the microwave field saturation caracteristics and the results of interaction of different gases (H_2, O_2, CO, CO_2, H_2O-vapours) with BeO-surface show that the observed narrow line belongs to the lectrons captured by oxygen vaconcy forming F^+-centers with $g_{F^+} = 2.0025, \Delta B_{F^+} \sim 0.42$ mT and the wide one belongs to the hole V^--centers with $g_{V^-} = 2.012, \Delta B_{V^-} \sim 1.2$mT. In spite of difference between plasma forming air or oxygen media, the nature of localized states

remains identical Figure 1a and 1b. Only the intensities of lines according to spectra of F^+- and V^--centers change ($N_{pc} = N_{V^-} + N_{F^+}$). It is natural that the concentrations of these centres also change.

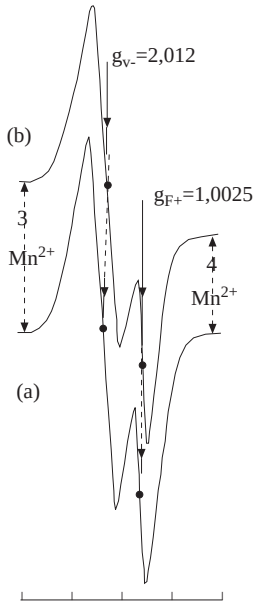

Figure 1. EPR spectrum of BeO exposured by Ed in air (a) and in oxygen (b) at 77K; E=$2.5 \cdot 10^6$ V/m, P=13,3 Pa, 3 and 4-the lines of the basic standart of Mn^{2+} in MgO

Significant difference is observed in the kinetic regularities of accumulation of localized charges for various plasma forming media. In oxygen plasma the relation $N_{pc} = f(t)$ monotoicly rises and has a maxima of $t = t_{\max}$ (Figure 2, curves 1-3 and $1'$-$3'$), then the dip of curves and their stabilization are observed ($at - t > 45 - 60$ min). For these curves the kinetics of accumalation of F^+-and V^--centers is described as a sum of two relations:

$$N_{pc}(t) = N^{\circ}_{pc}(t) + N'_{pc}(t). \tag{1}$$

In the region of $t < t_m$ the kinetics of PC-formation is described by the expression:

$$N^{\circ}_{pc}(t) = N_m/2\{1 - \exp[-A(t - t_m)K]\}. \tag{2}$$

After $t \geq t_m$, the PC concentartion decreases and the relation $N_{pc}(t)$ has approximately the following form:

$$N'_{pc}(t) = N_m/2\{\exp[-A(t-t_m)K' + 1]\}, \qquad (3)$$

where $N^{\circ}_{pc}(t)$ and $N'_{pc}(t)$ are the current and N_m is the maximum value of PC-concentration; K and K' are the PC-formation constants depending weakly on discharge power $A(E/P)$; and m is a constant reflecting the location of maxima with respect to the stationary values of N_∞.

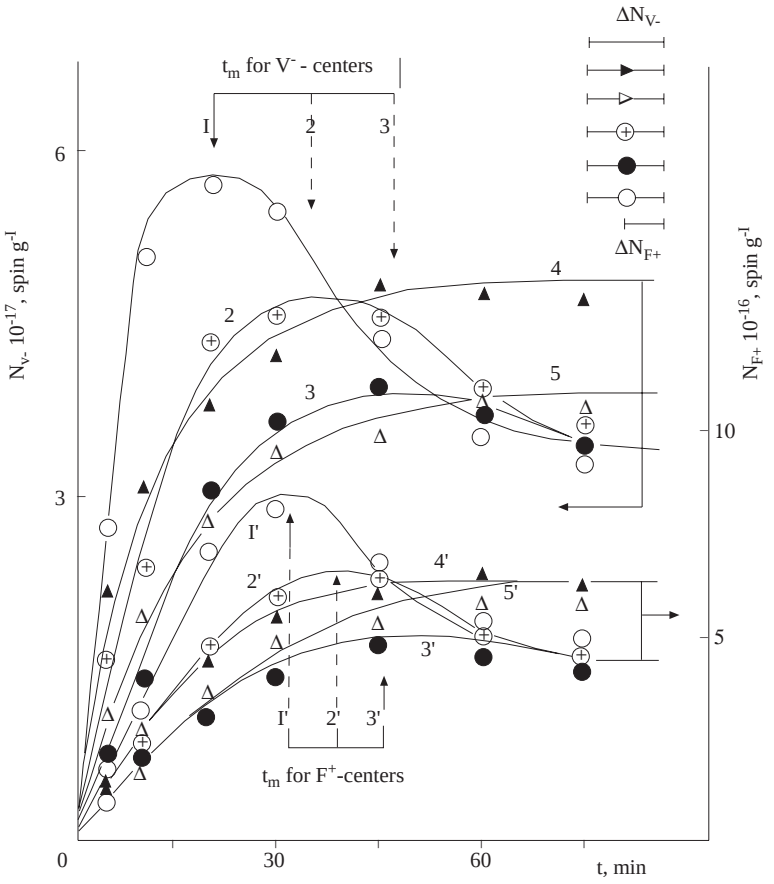

Figure 2. The accumulation kinetics of hole V^- (1-5) and electron F^+ (1′-5′)-centers in BeO under electric discharge action in oxygen (1-3 and 1′ -3′) and in air (4,5 and 4′, 5′) at 77K; E=2.5·10^6 V/m, P=1,3 (curves 1,1′); 1.3·10^2 (2, 2' and 4,4′) and 1.3·10^4 (3,3′ and 5, 5′) Pa

From comparison of (2) and (3) it follows that $K \neq K'$ since K' includes the thermal effects connected with the arising of the local heating due to the discharge process of BeO, i.e. $K' = K + K_\tau$ where K_τ is the thermal annealing rate constant.

The main distincition between the accumalation kinetics of F^+- and V^--centers in oxygen and air is the presence of extremes in $N_{pc} \sim f(t)$, their gradual smearing at incresaing of O_2 pressure and a complete disappearance at $E/P < 2 \cdot 10^2 V/m \cdot Pa$ (Figure 2, curves 3 and 3'). And in this case, the drift of the maximum of the hole V^--centeres is faster than that of electron F^+-centers. Moreover, for large discharge exposure times the blending of curves in the stationary region and the coincidence of concentrations of F^+- and V^- centers at various E/P are observed. The behaviour of the relation $N_{pc} \sim f(t)$ in air plasma conditions considerably changes from that in oxygen plasma (curves 4,5 and $4'$, $5'$). On kineic curves, the extreme values of N_m are not manifested and the relation $N_{pc} \sim f(t)$ is described by a montonically increasing function (2) with different stationary values of N_∞ mainly for V^--centers with various E/P.

It is also observed that the decreasing of the formation rate, mainly of V^--centers in oxygen media, is 1,5 times less than that in air for the same E/P (curves 2,3 and 4,5). For F^+ centers in oxygen plasma, the difference between their formation rates is small and these rates are nearly a like in values (curves $2'$, $3'$ and $4'$, $5'$). Futher, the behaviour of $N_{pc} \sim f(t)$ for $t \to \infty$ for both media is almost similar, i.e. the concentration stabilizes in a stationary region of kinetics.

It should be noted that for discharge in air the similar behavior of kinetic curves of PC-accumulation as in oxygen is not detected. Moreover, in non-purified oxygen plasma forming media the deviations of observed kintic laws of accumulation of localized charges in BeO under the influence of ED are showed.

4. Discussion

Before te discussion we must note some features of mechanism of elementary processes in gas discharge plasma [16-18] connected both with generation of excited and ion states [17,18] and with photons emitted by a recombination of unlike charges particles in the plasma forming medium. That is, emission plays a natural and special role both for the periodic recurrence of excitation and ionization of the medium and that it is presential for constant current flow in plasma forming media and for photostimulated or photochemical processes. When there is a heterogeneous system the investigation of photosorption and photocatalytic processes on the surface of solid, including BeO [19, 20], is the subject of the extra researches and a role of emmiting photona in plasma processes is not denied.

The main aim of this investigation is to reveal the efficiency of processes that give rise to the activation of the BeO surface by the charged and neutral oxygen particles. Therefore, the similarity law of gas discharges and the main particles of phasma forming medium must be taken in account. According to [17, 21] the electron energy of discharge in oxygen medium is much more than the ionization potential, i.e. $I < W_e \sim 20$ eV under our conditions it corresponds to value of $E/P = 2 \cdot 10^4 V/m \cdot Pa$) It must also be noted that besides electrons and exited states there are also oxygen atoms, stable $(O^+, O^-, O_2^+, O_2^- \ldots)$ and unstable $(O_3^+, O_3^-, O_4^+, \ldots)$ ions. The concentration of these

or other oxygen ions depends on the discharge power or E/P, and gas temperature; and these oxygen concentrations are well enough controlled by these parameters. For instance the number of electrons N_e having the energy W_e and concentration of monoatomic axygen ions decrease with $E/P < 10^4 V/m \cdot Pa$ (at E= const). Simulataneously, the concentration fractions of molecular oxygen ions $(O_2^+, O_2^- \ldots)$ and the local heating time in the surface pores where the microdischanges occur are increasing.

These microdischarges developing in pores between the surfaces of BeO grains are one of the factors acting on a change of the concentration of localized charges in the oxide dielectric. However ar E/P increases, the number of electrons N_e both with an energy $W_e > I$ and that of monoatomic oxygen ions (O^+, O^-) increases. But it is not denied the formation of localized states in discharged BeO. The nature of these states is similiar to the of electron F-and hole V-centers [22,23] which are the anion and cation vacancies that trap two electrons and two holes, respectively, including also their nonparamagnetic states.

Theref ore, the treatment of BeO in oxygen causes the destruction of the localized F, F^+ and V, V^- states. The bulk interaction of oxygen plasma ions with unlike charged centers can be schematically given as follows:

$$
\begin{aligned}
&V^-(V) + e^- \xrightarrow{K_1(K_1')} V^{2-}(V^-) + [e_{st}^+ + e^-] \rightarrow V^{2-}(V^-) + h\nu_1 \\
&V^-(V) + 0^- \xrightarrow{K_2(K_2')} V^{2-}(V^-) + 0 + [e_{st}^+ + e^-] \rightarrow V^{2-}(V^-) + 0 + h\nu_1 \qquad (4) \\
&V^-(V) + O_2^- \xrightarrow{K_3(K_3')} V^{2-}(V^-) + O_2 + [e_{st}^+ + e^-] \rightarrow V^{2-}(V^-) + 0_2 + h\nu_1,
\end{aligned}
$$

$$
\begin{aligned}
&F^-(V) + e^- \xrightarrow{K_4(K_4')} F^{2+}(F^+) + [e_{st}^- + e^+] \rightarrow F^{2+}(F^+) + h\nu_2 \\
&F^-(V) + 0^+ \xrightarrow{K_5(K_5')} F^{2+}(F^+) + 0 + [e_{st}^- + e^+] \rightarrow F^{2+}(F^+) + 0 + h\nu_2 \qquad (5) \\
&F^-(V) + O_{2^+} \xrightarrow{K_6(K_6')} F^{2+}(F^+) + O_2^- + [e_{st}^- + e^+] \rightarrow F^{2+}(F^+) + h\nu_2,
\end{aligned}
$$

where $K_i(K_i')$ are the constants of rates in respective reactions; V^- and F^+ are the para-and diamagnetic localized states; $e^+ = [e^-]$ is the free elementary positive charge in the dielectric; and $[(e_{st}^+)e^+ + e^-(e_{st}^-)] = h\nu_i$ is the radiation energy emitted by the recombination of localized holes (electrons) with free negative (positive) charges.

For both plasma forming media the relative (approximately difference 1,5 times) formation rates of PC in the iniial region of the curves (Figure 2, curves 2,3 and 4,5) is connected with an increased probablity of interrecombination destruction of PC in localization centers. So, the destruction of localized states in oxygen is stronger that that

in the air due to additional influence of mechanisms (4) and (5), confirmed experimentally by the kinetics. Further, independently of power A(E/P) and discharge interaction times, the PC concentration stabilizes both in air and oxygen. It has been seen from equations (1) and (3) for $(t - t_{\max} \to \infty$ that $N_{pc}(t) = N'_{pc}(t) = N_m/2 \to N_\infty$. But the kinetics in air plasma hos no accumulation curves extremes of localized charges ot $t = t_m$ (curves 4,5 and $4'$, $5'$).

In oxygen media, as compared with air, the physico-chemical picture of plasma states, depending on oxygen pressure significantly changes due to the formation of low and high gradient discharge forms, which sharply differ with the intensity of electric field [10,11]. Both forms of discharge in oxygen differ also in chemical activity: in low gradient form, the molecular ions O_2^+ and O_2^- mainly predominate; and in high gradient form, the ions O^+, O^- and oxygen atoms prevail. These oxygen particles are the main factor causing the differences in kinetics of PC-accumulation ind dependence on physico-chemical medium properties. So, their presence and role in air are small, since their lifetime is less than the discharge investigation period. Evidently, on the one hand, it is connected with a compensation of oxygen particles by impurities present in air, such as $H_2, CO, CO_2, NO, NO_2, N_2O \ldots$ and H_2O vapours, and, on the other hand, with the small oxygen content in the air medium. Each of these components and their radical forms have various influence on the surface of the dielectric. As such, in the same air-oxygen mixture, some particles will reduce white others will stimulate the process of PC localization in BeO, when discharged, and brings to the stabilzation of PC concentration in a stationary region of kinetics.

However, in different gas mixtures or air plasma the various effects (e.g. the thermal Frenkel effect) are not detectable due to the superposition and the merging of some side effects connected with elementary physical-chemical processes which take place in the gas discharge. But in pure plasma forming media, particluarly in oxygen, the thermal effects are indirect, but show sharply. It is connected the characteristic that in oxygen plasma only, ions and radicals are interstitial active particles. In fact, from the kinetic curve (Figure 2) one can see that, near the maximum PC accumulation curves, indications of the thermal effect are appearing, and at $t = t_m$ the equilibrium between the processes of formation and destruction of localized states has its begining. It also follows from forulas (1)-(3) that at $t = t_m$ for which we have $N_{pc} = N_m$.

Moreover, theidentity and nature of localized charges in BeO generated by the interaction of ED' leads independently of air and oxygen properties (see Figure 1) to the formation of the surface charge state on the BeO surface [5,6], i.e. of the electric field (Pool-effect). The later is the sufficient codition for the charge of such physical and physical-chemical properties as adsorbtion and desorbtion equilibrium and also katalitical and dielectrical properties of BeO dielectric.

THerefore in an oxygen plasma forming medium, the observations of simultaneous drift and non-coincidence of maximum values of PC-concentration N_m for various E/P (or various P at a constant E) are explained according to the Pool-Frenkel effect, which is not observed in air. Thus by discharge exposure the existence of the electrical field

and the local heating of the BeO surface not only stimulate the release of trapped NCC and their transition into delocalized states but also provide their drift: the electrons drift to surface and the holes drift in oppositie direction. The mechanism arising from this process lies in the following: at a constant E, by changing oxygen pressure the free path length (λ) of bombarding oxygen particles Dispropotionaly change and, accordinly, their energy acquired along the strongly heterogeneous discharge field E also changes. It takes place in conformity with the relation $W_e \sim e\lambda_e E \sim P^{-1}$ (E_d is always less than E). By analogy with this, both the energy of photon emittion by the recombination of positive and negative oxygen ions and the grade of heating of the BeO surface depending on O_2 pressure dielectric discharge time are changing. The manifestation grade and the running mechanism of this elementary process are spontaneously regulated by the discharge power, or parameters E/P. So with decreasing P or increasing $E/P < 2 \cdot 10^2 V/m \cdot Pa$ N_e with energy $W_e > I_i \sim 13,6$ eV, the number of most mobile monoatomic oxygen ions O^+ and O^- are increases while the mean heat propagation rate and the plasma energy are decrease due to the reduction of concentration of heat in a limited space interval, mainly in those regions where the microdischarges develop.

However with increasing $P, E/P < 10^4$ $V/m \cdot Pa$ decreases and causes opposite effects: the number of inertial molecular ions $O_2^+, O_2^- \ldots$, exhibits large incerases due to the adsorbtion of electrons to the neutral particles or the desorbtion from ions of plasma forming medium and the discharge fully trans forms into its lowgradient form. For this form of discharge, due to low mobility of ions $O^+, O_2^- \ldots$ and neutral O_2 molecules both the density of oxygen particles and their collision frequency probability increases. Each collision of these oxygen particles is accompanied by an interchange of certain energy portions exceeding silghtly the mean plasma particle energy which provides the condition for the transition from non-equilibrium of discharge process to quasi-exuilibrium state.

In such cases the propagation of heat and energies within a microdischarge space "goes ahead" of the drift of electrons and ions along the field. Further, the desorbtion or adsorption of ions to the BeO surface and their interaction with V^-, V-and F^+, F-centers according to the mechanisms (4) ahr (5) takes place. The interaction is simultaneously accompanied by emition of electrons and ions [24, 25]. Therefore, under conditions of quasi-equilibrium state the generatiopn process of localied PC's in BeO is partially supressed by the influence of emission and of thermal-field Pool-Frenkel effect causing not only the stabilization of PC- concentrations but also the gradual smearing and disappearing of maxima in a stationary region of kinetics ($t > t_m$), from which comes equilibrium of these two processes due to theri mutual compensation.

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