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Modified Humidity-Sensitive Ceramics For Microelectronics Studied By PALS System

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***Abstract* — Water-adsorption and desorption processes in the modified functional elements based on humidity-sensitive MgO-Al_2O_3 ceramics for microelectronics were studied using specialized positron annihilation lifetime system. It is shown that adsorption of water leads to transformation of positron annihilation spectra in the MgO-Al_2O_3 ceramics and reflects increasing of positron trapping near grain boundaries of ceramics and ortho-positronium decaying in nanopores. Fixation of positron lifetime components results in changes in positron trapping rate.**

Keywords* — *positron annihilation system; spectroscopy; water-sorption process; structural analysis

I. INTRODUCTION

It is well-known that functional MgO-Al_2O_3 ceramics are more stable in compare with other porous materials with short time to humidity changes [1-3] and can be used as humidity-sensitive elements in microelectronics [4,5]. It is shown that functionality of such materials is appointed by microstructure of grain boundaries, grains and pores in ceramics [6]. In addition, the functional properties of elements sensing to humidity depend on water-sorption properties in their materials. Moreover, there are problems connected with preparation of nanoporous ceramics with controlled specific surface area, amount of open porosity, optimal pore size distributions and inner free volumes [6]. Thus, free-volume properties in MgO-Al_2O_3 ceramics prepared at different conditions and influence on their functionality should be studied carefully.

Previously, we studied the effects of surface area on initial Mg and Al oxides on the structural properties of $MgAl_2O_4$ ceramics prepared at 1100-1400 ^oC [7-9]. It was shown, that the formation of the main spinel $MgAl_2O_4$ phase is intensified with rise of sintering temperature and duration of ceramics preparation [9]. Functionality of spinel ceramics depend on their porous structure prepared and different time-temperature conditions.

Commonly, microstructural properties of ceramics is probed by X-ray diffractometry, porosimetry, electron microscopy, etc. [10-12]. But to obtaining more information on sorption processes in modified functional MgO-Al_2O_3 ceramics the new approaches and methods for structural analysis should be developed. One of such methods is positron annihilation lifetime spectroscopy (PALS) [13,14], known experimental tool to investigation of open and closed free volumes and defects in solids independent on their structural hierarchy [13]. The aim of this work is investigation of water-moisture processes in the modified MgO-Al_2O_3 ceramics using specialized PALS system.

II. EXPERIMANTAL

The investigated functional MgO-Al_2O_3 ceramics were sintered using conventional procedure as was presented elsewhere in [7-9,15]. The obtained samples were sintered at temperatures (T_s) 1100 ^oC, 1200 ^oC, 1300 ^oC, 1400 ^oC for 2 h. Final humidity-sensitive ceramics are characterized by tri-modal pore-size distribution with radiuses of open pores of ~0.003, 0.01-0.09 and 0.3-0.4 μm [7,9].

The PALS spectra for as-prepared samples were recorded at temperate of 22 ^oC and relative humidity of 35 % as well as after water-immersion using specialized ORTEC system [7-9,15,16]. Two identical samples were placed in sandwich structure for PALS measurements. Every spectrum was investigated with channel width of 6.15 ps. Isotope ^{22}Na was exploited as positrons source.

The selection of corresponding values for measuring chamber permit to investigation of samples at constant values of *RH* in the range of 25-60 % with an accuracy of ± 0,5 % and 25-98 % з with an accuracy of ± 1 %. Analysis of the PALS data were performed using three-component fitting procedure, in some cases at fixation of the first and second positron lifetimes using LT computer systems [17]. PALS

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spectra decomposed on three components with τ_1, τ_2 and τ_3 lifetimes as well as I_1, I_2 and I_3 intensities are shown in Fig. 1.

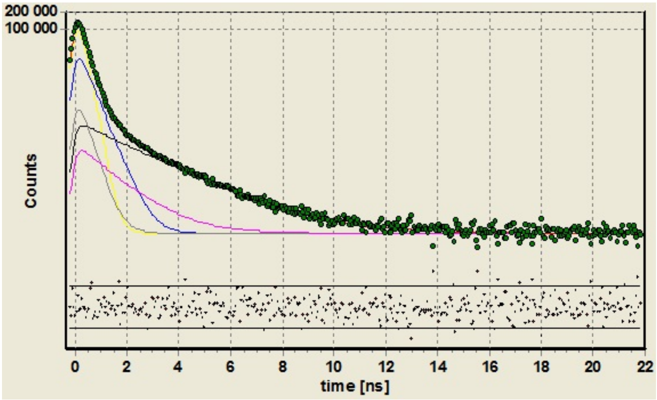

Fig. 1. Fitting of PALS spectra on three components using LT program for the modified $MgO-Al_2O_3$ ceramics sintered at 1300 °C

In addition, using two-state positron trapping model [18,19] positron trapping rate in defects (κ_d), positron lifetime in defects (τ_b) and average positron lifetime ($\tau_{av.}$) were calculated.

III. Results and discussion

The obtained PALS characteristics for the modified $MgO-Al_2O_3$ ceramics sintered at different T_s have a peak and region of smooth fading of coincidence counts in time (Fig. 2). Mathematically such curves describe by sum of exponential functions with different indexes (inversed to lifetimes).

As has been shown early [7-9, 15,16], the first component of PALS spectra with lifetime τ_1 and intensity I_1 as well as the second component with lifetime τ_2 and intensity I_2 are related to positron trapping modes. The lifetime τ_2 reflects positron trapping on defects located near grain boundaries on ceramic materials.

In as-prepared ceramic samples obtained at different T_s, the shortest τ_1 and middle τ_2 positron lifetimes and intensities I_1 and I_2 reduced with rises of sintering temperature (Fig. 3). In spate of structural distinction of ceramics sintered at different T_s, positrons are trapped in defects with the same rate of $\kappa_d = 0.60$ ns^{-1}.

The third PALS component with lifetime τ_3 is connected with ortho-positronium (o-Ps) decaying. In initial (as-prepared) ceramic samples this lifetime reduce from 2.6 to 1.9 ns with T_s, but intensity I_3 is closed to 0.02. In water-adsorbed ceramics lifetime τ_3 is closed to 1,84 ns, while $\tau_3 \sim 1.88$ ns is related to o-Ps "pick-off" decaying in water at 20 °C. In all cases, intensity I_3 rises from 2 % to 12-15 % testifying large amount of adsorbed water in ceramic samples. This change is accompanied by reduced in parameters of the first PALS component, but parameters of the second component are without changes.

As demonstrated in [8], in water-adsorbed ceramics κ_d parameter increases from 0.6 ns^{-1} to 0.7 ns^{-1} in ceramics prepared at 1100 °C and to 0.9 ns^{-1} in ceramics sintered at 1200-1400 °C. This fact testify that water-adsorption in ceramics bulk influences on positron trapping rate in defects.

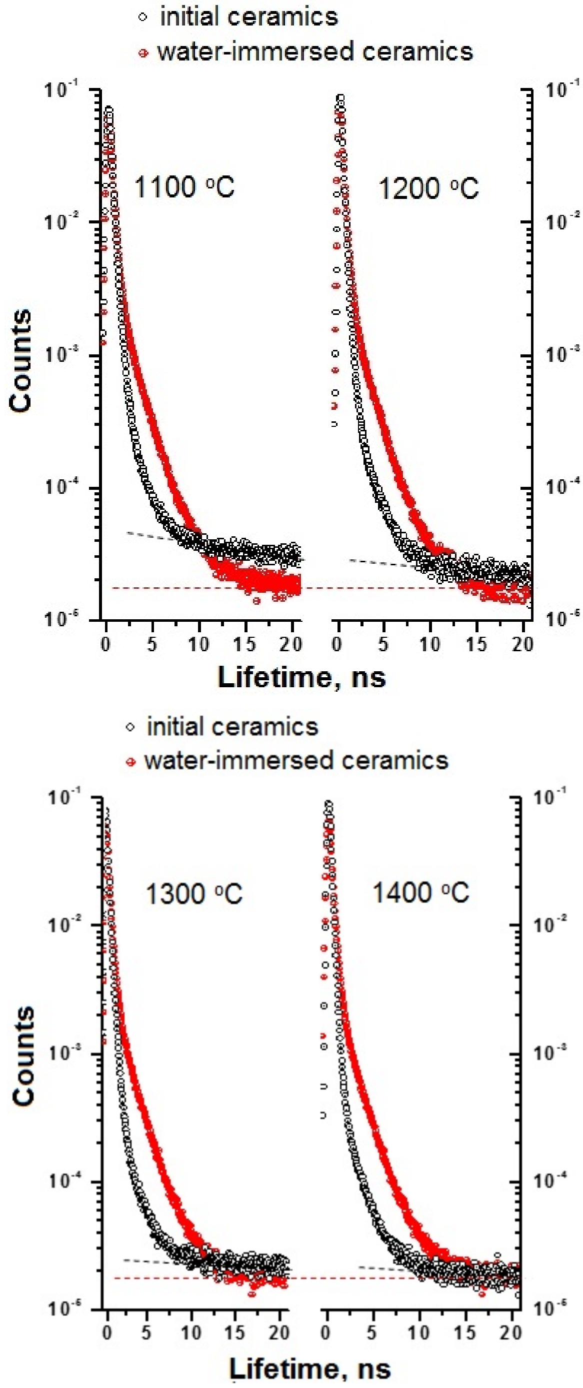

Fig. 2. Positron lifetime spectra for initial and water-moisture $MgO-Al_2O_3$ ceramics sintered at different T_s

Therefore, to study more considerable changes in positron trapping in the modified $MgO-Al_2O_3$ ceramics caused by absorbed water, the new algorithm is needed to treatment of PALS data. This task can be permitted due to fixation of τ_1 and τ_2 parameters because adsorbed water not changes structure of spinel ceramics.

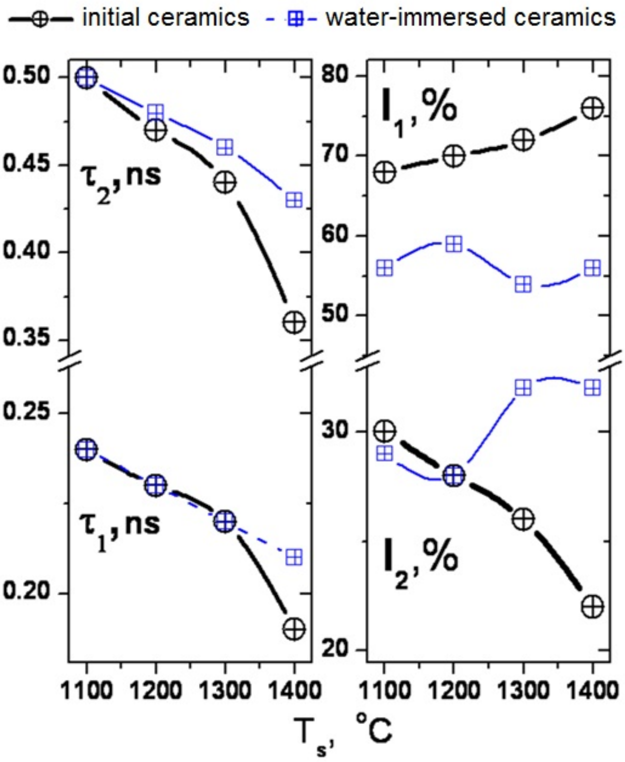

Fig. 3. Changes in lifetime components in dependence on sintering temperature of $MgO-Al_2O_3$ ceramics

As was shown early [25-28], the lifetime τ_2 is related to extended defects near grain boundaries in ceramic materials. Positrons are trapped in the same defects in $MgO-Al_2O_3$ ceramics independent on amount of adsorbed water by their nanopores.

So, the first and second positron lifetimes (τ_1 and τ_2) can be considered near constant. Therefore, all changes in fitting parameters of these components will be reflected in intensities I_1 and I_2. The third lifetime τ_3 is non-fixed. Treatment of experimental PALS data were carried out at fixed lifetimes (τ_1=0.17-0.2 ns and τ_2=0.36-38 ns). At that, the best FIT parameters were obtained at constant lifetimes τ_1 = 0.17 ns and τ_2 = 0.37 ns [7]. The I_1 and I_2 intensities are change dependently from amount of adsorbed water in $MgO-Al_2O_3$ ceramics. Thus, rising of relative humidity (*RH*) from 25 % to 98 % result in reducing of intensity I_1 and increasing of intensity I_2. The changes of *RH* from 98 % to 25 % reflects inverse to previously described transformation in I_1 and I_2 intensities (Fig. 4). The positron trapping in water-immersed defects related to the second component is more intensive. The lifetimes τ_3 are near 2.3-2.8 ns. The input of this component is not change and intensity is near 1 % [18].

In contrast, most significant changes in positron trapping in $MgO-Al_2O_3$ ceramics caused by water sorption reflect in positron trapping rate in defect κ_d (Fig. 4). Thus, the water-sorption effect in the studied spinel ceramics is accumulated in non-direct trapping κ_d parameter [7].

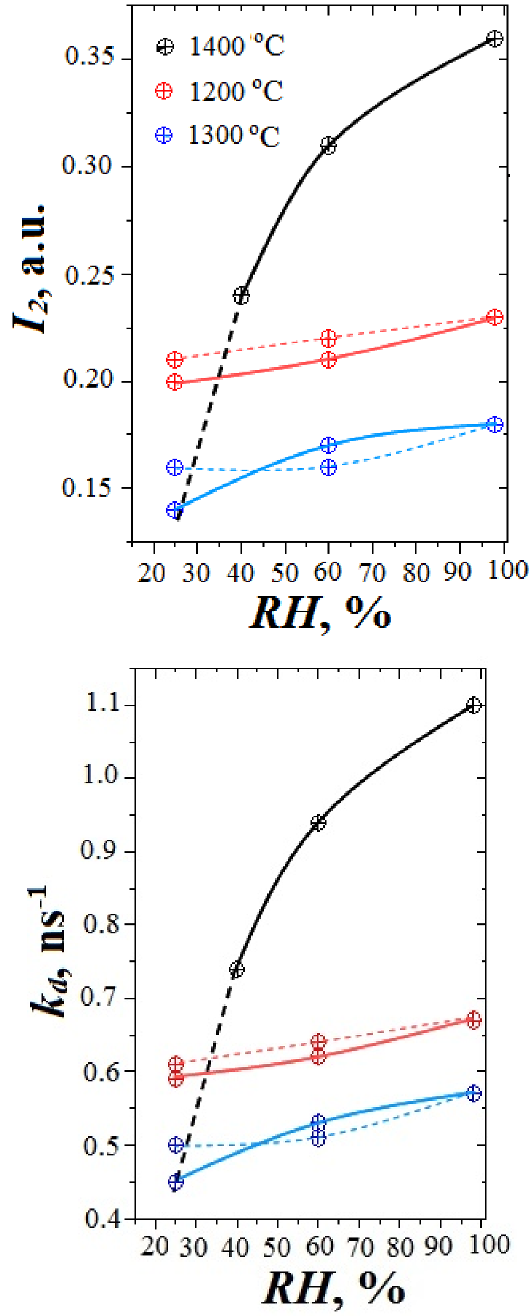

Fig. 4. Dependences of positron intensity I_2 and positron trapping rate κ_d on relative humidity in adsorption-desorption cycles for the $MgO-Al_2O_3$ ceramics sintered at different T_s

IV. CONCLUSIONS

Specialized PALS system is quite reliable method to study water-sorption processes in the modified $MgO-Al_2O_3$ ceramics. It should be noted, that in all ceramic samples (sintered at different temperatures with different microstructure and content of absorbed water) the same type of positron trapping defects prevails.

The positron trapping in defects occurs more efficiently in water-immersed ceramics due to increase in positron trapping rate of extended defects. The more perfect structure of ceramics, the more considerable changes occur in the water-absorbing pores.

The mathematical treatment of experimental PAL data at constant values of reduced bulk and defect-related lifetimes allow to refine the most significant changes caused by absorbed water in the functional ceramics.

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