MICROSTRUCTURAL ORIGIN OF THE DIELECTRIC BREAKDOWN STRENGTH IN ALUMINA: A STUDY BY POSITRON LIFETIME SPECTROSCOPY

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Abstract

The dielectric breakdown strengths of two series of sintered alumina samples (of low and high impurity content, with Si being the dominant element) and single crystals are compared with positron lifetime measurements. It is found that the breakdown strength increases linearly with increasing concentration of positron traps at grain boundaries. These traps are likely clusters containing negatively charged cationic vacancies, which are induced by silicon dissolution into Al_2O_3. Therefore, the improvement of the breakdown strength can be traced to silicon segregation at grain boundaries. A solubility of Si in Al_2O_3, achieved during the firing schedule of the sintering process, and which does not take into account enhanced solubility caused by mutual compensation of Si with other lower valence foreign cations such as Ca and Mg , is estimated at 120 ppm.

1. Introduction

Positron Annihilation Lifetime Spectroscopy (PALS) is sensitive to vacancy-like defects in materials [1]. In oxides, the dissolution of foreign cations, greater or lesser in valence than the host cation, requires that charged point defects be created in order to preserve electrical neutrality. Neutral and negatively charged vacancies (or vacancy clusters) act as positron traps. In Al_2O_3, only the cations greater in valence than Al, such as and Si, can induce negatively charged vacancies, namely the cationic vacancies V_{Al}''' [2,3]. In addition, the defect structure achieved during the firing schedule of the sintering process comprises, among other defects, isolated V_{Al}''' as well as neutral and negatively charged defect complexes containing cationic vacancies [3,4].

In previous work [4, 5], PALS measurements were carried out in two series of sintered Al_2O_3 samples. In both materials, Si was the dominant impurity (i.e., 90 ppm and 1500 ppm). Two lifetime components of 137 ps and 400 ps were resolved for both series, which can be interpreted as an indication that the natures of positron traps are identical in the two materials. The shorter lifetime was assigned to V_{Al}''' located within the grain and the other to grain boundaries clusters (i.e., likely V_{Al}''' associated with segregated impurities [4]). The dielectric breakdown strengths of the same sintered and of single crystals have also been reported [6].

The purpose of this work is to improve the understanding of the microstructural origin of the dielectric breakdown by calling for the nature and localisation of defects that are provided by PALS measurements. An earlier attempt to establish a relation between the breakdown strength and PALS measurements has been suggested [6]. Here, the *two state trapping model*, which considers only one trapping process, was used. In the present work, the results derived from a more complete description (i.e., *the three state trapping model* [7]) are utilised. This

description allows an access to positron trapping in defects located within the grain and at gain boundaries.

2. Materials preparation and experimental

2.1 Materials characteristics and preparation

The material referred below as doped samples contained SiO_2 (1497 ppm), MgO (723 ppm), CaO (686 ppm), Fe_2O_3 (415 ppm) and Na_2O (404 ppm). The other one considered as pure contained SiO_2 (90 ppm) Na_2O (40 ppm) and background impurities (of total amount near 20 ppm). Sintering was performed in air and the different grain diameters were reached by controlling the firing schedule [6].

2.2 Breakdown strength determination

The experimental set up and the measurement procedure were described in Ref [6]. The breakdown strength E_c as a function of specific surface of grain boundaries (s_{GB}) are plotted in Fig. 1. The specific surface is estimated by assuming grains of spherical shapes, i.e., $s_{GB} = 3/R$ where R is the mean radius of grains. For pure sample, E_c seems to be constant at value about 15.2 kV/mm whereas for doped ones a linear dependence $E_c = 0.454\ s_{GB} + 12.16$ kV/mm is observed. The value of the breakdown strength of a single crystal (12.3 kV/mm) is also given, which evidently corresponds to an infinite grain radius.

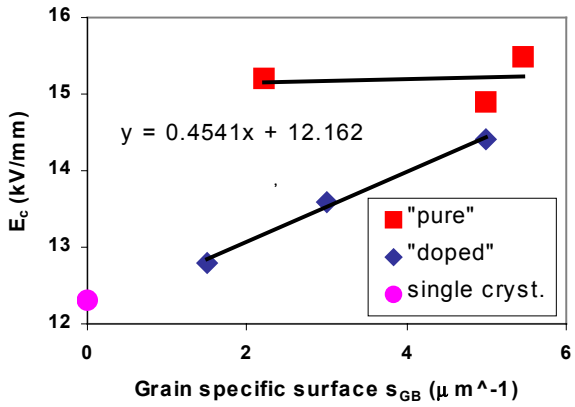

Fig 1.Breakdown strength versus specific surface of grains in alumina samples of different impurity contents.

2.3 Positron lifetime measurements : analysis and results

For the PALS experiments, the same single crystal and doped samples were taken as in the breakdown strength measurements. However, in the case of pure material, two other samples were used. These samples have the same impurity contents as those of Fig 1, but differ by their grain size [4]. The positron lifetime spectra were recorded at room temperature using a conventional fast-fast coincidence system. The spectra were measured in 2000 channels (calibration 27 ps/channel and FWHM of 270 ps) and collected about 6×10^6 counts. They were analysed via a *LT v.9 program* [8], in which *the three-state trapping model* [8] was introduced into the source code The three states refer to different locations of positron annihilation (i.e., in the bulk material, in vacancies within the grains and in defects at grain boundaries). In the case of doped samples, the first state (annihilations in the bulk) turned out to be negligible. In single crystal, the third process (annihilation at grain

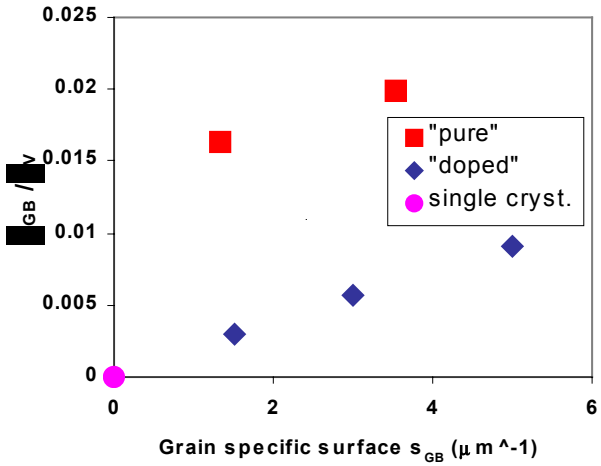

Fig 2.The ratio of positron trapping rates κ_{GB} / κ_V into defects at grain boundaries and into vacancies inside grains versus specific surface of grains..

boundaries) is considered equal to zero as there are no grain boundaries. The details of the experiments and their analyses have been described in our previous works [4, 5]. In Fig 2, the ratio κ_{GB} / κ_V (where κ_{GB} and κ_V are respectively the positron trapping rates in defects at grain boundaries and in defects within the grain) is plotted as a function of s_{GB}. Only these PALS spectrum parameters are of interest for the scope of this paper.

3. Discussion

From the comparison of Fig 1 and Fig 2, one can observe that the dependences of *Ec* and κ_{GB} / κ_V on s_{GB} are quite similar. This suggests a correlation between E_c and the ratio κ_{GB} / κ_V. According to the trapping model, this ratio is proportional to c_{GB} / c_V, where c_{GB} and c_V express concentrations of positron traps within the grains and at grain boundaries. The proportionality factor is expected to be of order of unit. For a given type of samples, c_V has almost a constant value, i.e. independent of the grain size [4]. Consequently, the variations of the ratio κ_{GB} / κ_V reflect, in fact, changes of the concentration of positron traps, c_{GB}, at grain boundaries. To determine the changes of $c_{GB} = const \times c_V \kappa_{GB} / \kappa_V$ the concentration c_V within the grains in pure and doped samples must be known.

For pure samples, c_V can be estimated, with some assurance, from the Si content, at about 28 ppm [4]. However, in the case of doped samples, c_V cannot be evaluated on the basis of impurity content, because it is so high that c_V achieves its ultimate value, which is determined by the solubility of Si. Assuming that the correlation between E_c and c_{GB} is the same for pure and doped samples, one could estimate the unknown value c_V for doped samples by fitting a straight line to all of the experimental points in the plot E_c against $c_{GB} = const \times c_V \kappa_{GB} / \kappa_V$ (Fig 3). The best fit can be obtained if c_V in doped samples is 40 ppm. Taking into account that a vacancy is induced by the dissolution of three Si atoms [4], one can estimate the "*apparent*" solubility limit of Si at 120 ppm (here it must reminded that Si is the only foreign element whose dissolution can give birth to negatively charged cationic vacancies V''''_{Al} and hence to positron traps [2, 3]). This value is lower than the solubility limit reported in Ref [9] and [10] under sintering conditions close to ours. There, Si level in the range 200-300 ppm was found just sufficient for the formation of glassy grain boundary films. We have to acknowledge that PALS cannot reflect the actual solubility limit of Si in the doped samples. Indeed, some fraction of silicon could be prevented from inducing V''''_{Al}, due to possible mutual compensation of Si with impurities of lower valence, such as Ca and Mg [10], which are present in substantial amount in the doped samples. Therefore, the departure of this "*apparent*" solubility limit (120ppm) from the actual solubility one (200-300 ppm) could be seen as an assessment of the mutual compensation effects, i.e., enhancement of Si solubility in Al_2O_3 induced by Ca and Mg).

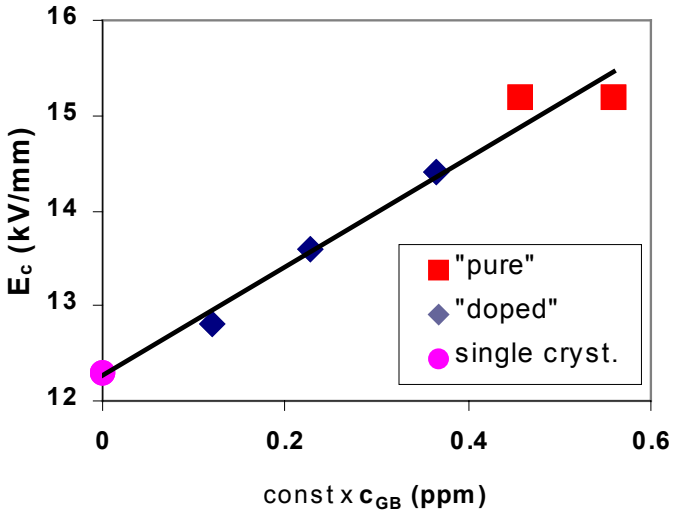

Fig 3. Breakdown strength as a function of defect concentration at grain boundaries. The straight line represents the best fit to the points (see text).

The correlation which emerges from Fig 3 indicates that the breakdown strength is improved by the existence of grain boundaries. However, its illustrates that such an improvement can be furthermore traced to the concentration of positron traps at grain boundaries. Since the positron traps are induced by Si dissolution into Al_2O_3, the breakdown strength is also sensitive to silicon segregation. Such a correlation appear as a signature of the effect of the microstructural development (generated during the sintering process) on a macroscopic property, i.e. the dielectric breakdown strength. However, a relevant question arises (i.e., Why the concentration of positron traps seems higher in the pure samples than in the doped ones as it appears in Fig 3 ?). Here again, mutual compensation effects could be responsible. Furthermore, preferential segregation of other foreign elements, and in particular of Ca which has the highest enrichment ratio [11], could reduce the concentration of Si at grain boundaries. Finally, one cannot exclude the formation of glassy grain boundary films. In any case, further clarification of this question requires investigations using several series of materials of well defined impurity contents. To this end, this work provides a framework, which can also be geared to the optimisation of the dielectric properties of sintered alumina.

4. References

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