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Study of charging phenomena in MgO single crystal: effect of polishing, annealing temperature and crystallographic orientation

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Abstract

Several experiments have shown that dielectric improvement of ceramics could be partially explained by the decrease of the trapped charge density. To carry out the study of charged dielectrics through to a successful conclusion, preliminary analyses are necessary to establish standard norms of utilisation of ceramics. Through recent studies, it was admitted that a trapping phenomenon is taking place on specific sites: point defects (impurities, vacancies...), lattice distortion and extended defects (grain boundaries, dislocations...) etc. Model of impurities states and Anderson states can analyse respectively the trapping and the diffusion of charges in ceramics. The aim of this paper is to outline the polishing effect on the charge trapping phenomena in a single crystal of magnesium oxide (MgO). In this way, using a scanning electron microscope (SEM), the charging phenomena was characterised for MgO as polished or post-annealed. In addition the role of the crystallographic orientation was studied. The amount of trapped charge is determined using the mirror method associated with the absorbed current method. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Crystals; Defects; Dielectric properties; MgO; Trapping

1. Introduction

Ceramics are well used in high technological devices. They are chosen because of their electric properties of insulation and their thermal properties. The main problem with ceramics is the trapping phenomenon of electric charges. Indeed, it was confirmed that breakdown,[1] fracture and wear are the consequence of dielectric relaxation which follows charge detrapping.[2] On the other hand, it is known that polishing of MgO introduces subsurface mesostructure, stable below 1300 °C,[3] constituted by dislocation network capable of charge trapping stable below 1300 °C. The same result was observed for alumina.[4] Thus, it is not sufficient to specify a dielectric by its macroscopic properties alone (e.g. permittivity) and its atomic properties (crystal structure); a mesoscopic analysis (grain structure, dislocation structure, etc.) is needed to characterise the trapping phenomenon.[5] From the physical point of view, the effect of disorder in the solid insulator is to produce localised states called Anderson states.[6] In this way, impurities, defects and disorder responsible for charge localisation do not have the same effect on charges; there is a hierarchy of localisation.[7] Disorder causes a weak localisation introducing localised states in the tails of the conduction band. The bandwidth of localised states depends on the degree of disorder: the more important the disorder is, the wider the localised states bandwidth is. On the other hand, a strong localisation, resulting from chemical species and certain defects such as vacancies and dislocations,[2,5] causes complete stabilisation of charge introducing states in the forbidden band, called impurity states. The energy bandwidth of the impurity states depends on the concentration of the considered defect. Only states lying in the impurity band can really constitute trapping states. This hierarchy of localisation provides a way to understand both conduction and trapping properties of the dielectric. The main point is

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that the defects, generating impurity band, are located in sites which are generally distributed at random in space. Resulting from this disorder is a certain broadening of the impurity band and an Anderson localisation. The important consequence of this localisation is that an electron can move from an impurity state to another only by exchanging energy with phonons.[6]

The investigation of charge trapping deserves attention because there is a link between the charging ability and the material properties.[1] It has been observed[8] and simulated[9] that pure MgO does not trap charges. But, whatever the elaboration method, MgO can contain several defects particularly point defect due to impurities and dislocations. Therefore, Vallayer et al.[8] has studied the effect of two types of surface defect: structural surface defects due to the cleaving process which are removed after annealing at 1500 °C for 4 h in air, and contamination layers which are removed at 300 °C for 2-h in a vacuum. In this paper, the charging ability of polished MgO as a function of annealing temperature and crystallographic directions is discussed.

2. Characterization techniques

When an insulating material is bombarded by electrons with sufficiently high energy, electrons can penetrate few atomic layers and generate excitons (electron-hole pairs). These electrons and holes may recombine, either leading to secondary electron emission or being trapped on defects. In this way, our experiments are based on two complementary methods employing a scanning electron microscope (SEM): the mirror method[8] and the absorbed current method.[10] These two methods have widely proved their efficiency in studying the charge properties of ceramics and allowed us to demonstrate that charging properties depend on the ceramic preparation and annealing temperature.[11] In the following we describe these two techniques.

The mirror method[8] is performed in two stages: first, a quantity Q_i of charge is injected with an electron beam of high energy. If secondary electron emission yield σ is smaller than unity[8] a net negative charge is trapped in the insulator; this trapped charge Q_p is supposed to be a point charge. Assuming now, that a point charge Q_p is implanted in a semi infinite dielectric and using the electrostatic image method,[12] the potential V created in the vacuum by this charge trapped in a dielectric with a relative permittivity ε_r, is equivalent to that created by a charge KQ_p placed in the vacuum.

$$V(R) = \frac{KQ_p}{4\pi\varepsilon_0 R} \quad (1)$$

where $K = \dfrac{2}{\varepsilon_r + 1}$.

The second stage is the formation of the mirror image: the field built by the trapped charges deflect electrons of low energy as a convex mirror does with light. As a consequence, an image appears on the screen showing some details of the SEM chamber. The centre of this image is a black spot of diameter d (see Fig. 1. This is the image of the last output diaphragm of the electron column of diameter d'.

A theoretical dependence of diameter d as function of the equipotential radius R is established by Vallayer et al.:[8]

$$\frac{1}{d} = \frac{4L}{d'}\frac{4\pi\varepsilon_0}{KQ_p} \quad (2)$$

where L is the working distance.

In the conditions of a semi infinite dielectric and of a point trapped charge, the slope of $V(1/d)$ curve can be used to estimate the quantity of trapped charge Q_p.

An insulator irradiated by an electronic beam of intensity I_i is the seat of the secondary electron emission which is defined by the total secondary electron emission yield σ:

$$\sigma = \frac{I_i}{I_\sigma} \quad (3)$$

where I_σ is the intensity of the total secondary electron emission current.

At high energy, the total secondary electron emission yield in an insulator is less than unity.[8] Therefore, the dielectric traps negative charges and an electric field is created in the vacuum of the SEM chamber. According to the electromagnetic laws a positive electric charge appears in all conductor pieces of the SEM chamber (mainly in gun and in the sample holder). This influence charges vary with the trapped charges. In fact, the created positive charge corresponds to an electron flux going from conductor pieces toward the ground. We can then collect the associated current, which is called absorbed current, noted I_{ab}. According to the principle of current conservation, the relation for currents is:

$$I_i = I_\sigma + I_c + I_{ab} \quad (4)$$

I_c is the flux of electrons conducted through the insulator to the holder. *I*n our study, we are interested in the measurement of the current produced only by the influence charge (I_c is considered negligible for wide samples). During the injection, the influence charges vary with the amount of trapped charges, therefore, it is possible to follow the evolution of the trapped charge and the absorbed current is found proportional to the quantity of the trapped electrons:

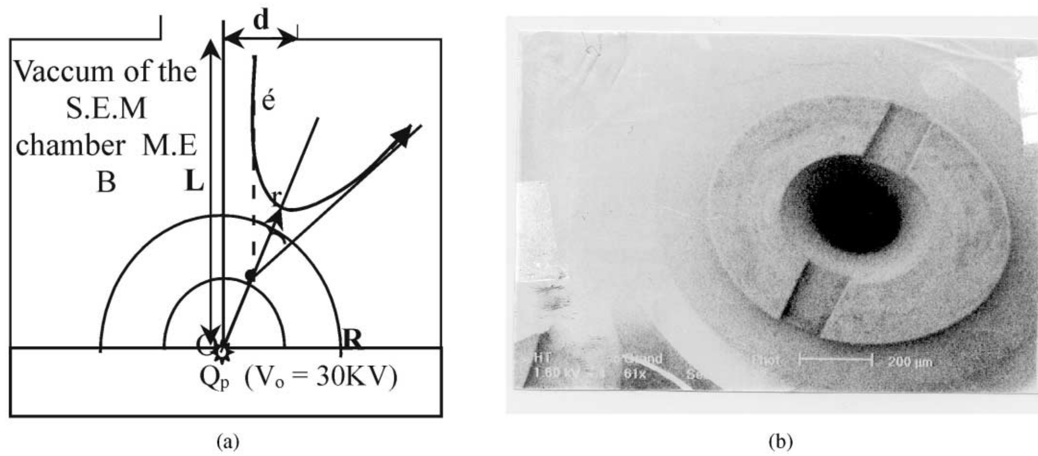

Fig. 1. (a) Principle of mirror image formation; (b) typical mirror image.

$$I_{ab} = \alpha \frac{d}{dt} Q_p \quad (5)$$

where α is the influence coefficient.

Experimentally, I_{ab} is only measured between the sample holder and the ground, as shown in Fig. 2(a), thus α is slightly less than unity. The expression of influence charge Q_{ab} is given by:

$$Q_{ab} = \int_0^{t_i} I_{ab}(t) dt \quad (6)$$

where t_i is the injection time. This leads to rewriting the Eq. (5):

$$Q_{ab} = \alpha Q_p \quad (7)$$

Let us consider the trapping yield π which is equal to Q_p/Q_i, where Q_i is the injected charge. According to the principle of charge conservation the trapping yield and the secondary electron emission yield are related by:

$$\pi + \sigma = 1 \quad (8)$$

In our study we are interested in the measurement of the trapping yield π.

Fig. 2(b) represents the variation of the absorbed current versus the time. It shows that the absorbed current is the highest at the injection starting. This initial current, noted I_{max}, represents the trapping ability of materials without any perturbation. I_{max} defines the intrinsic trapping ability and as was shown in Ref. 10 the intrinsic trapping yield ($\pi_0 = I_{max}/\alpha I_i$) is complementary to the intrinsic total secondary electronic emission yield σ_o.

The quick decrease of the current is due to the rise of a negative electrical field induced by the trapped charges, the internal field acts against the trapping. Then, the internal negative potential increases the energy of trapped electrons. Charges will diffuse and then localised in traps corresponding to their energy. Therefore, the zone concerned by the trapping phenomenon gets larger. The decrease of the absorbed current thus depends on the diffusion and recombinaison processes. In conclusion, the more punctual the distribution of trapped charges is, the sharper the slope of $I_{ab}(t)$ curve is.

3. Material and experimental protocol

The aim of our experiments is to study the charging phenomena as a function of annealing temperature and crystallographic orientations of MgO single crystal after polishing. Two sets of samples are used: a set with [100] direction, another with [111] direction. The samples are polished and supplied by the European Transactions and Promotions Society. The (100) face corresponds to the cleaving face and (111) surface is not well defined inducing probably multiple faces. Polishing leads to the creation of subsurface defects, such as dislocations.[3,4] In oxides, dislocation density is typically 10^4 dislocations/cm^2 (virgin crystal), after solicitation this density becomes 10^9 dislocations/cm^2.[13] In addition to subsurface defects, contamination layers can modify the charge insulating properties.[8] To carry out our study of polishing effect in MgO through a successful conclusion, an experimental protocol should be followed.

After cleaning with alcohol, samples are mounted on the sample holder inside the SEM (LEO 440). Heating in situ at 300 °C for 2 h is performed to remove contamination layers. Before electron injection, several conditions have to be fixed, such as beam focusing, choice of working distance etc. The injection is achieved by an energetic electronic beam of 30 kV. We must indicate the primary injected current I_i and the injection time t_i. Absorbed current is recorded during electron injection. Finally, after electron injection, the diameter d

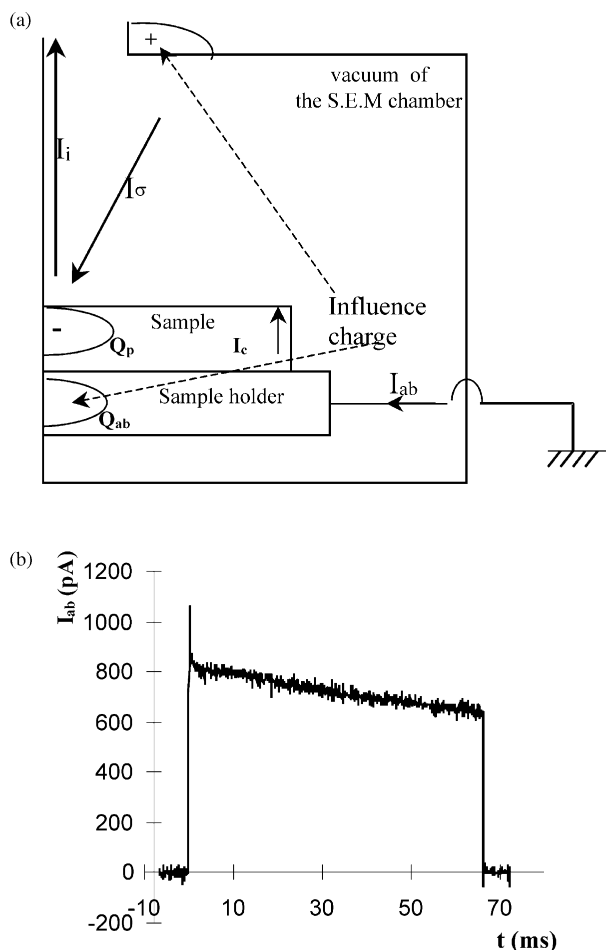

Fig. 2. (a) Principle of the absorbed current method. (b) Absorbed current typical curve for our sample.

of the black spot seen in the centre of the mirror image [Fig. 1(b)] is measured for each value of the potential V. The slope of $1/d\ (V)$ curve gives the quantity of trapped charges Q_p according to Eq. (2), and the integral of $I_{ab}(t)$ curve gives the quantity of influence charges Q_{ab} according to Eq. (6).

4. Results

4.1. Polishing and annealing temperature effect

In order to study the link between defects and trapping ability of polished MgO, two annealing temperatures are proposed: 1000 °C for 2 h and 1500 °C for 4 h. After heating in air, each sample is treated as indicated in the protocol above, while specifying that the primary beam is focused on the sample surface, with a primary current of 1.6 nA; working distance L is equal to 10 mm. In order to obtain different values of injection charge, the primary current was maintained constant and the injection time was variable.

In Fig. 3 is shown the variation of trapping yield π versus the quantity of injected charge Q_i for different annealing temperatures. From this figure both the MgO annealed at 1000 °C/2 h and the as-received one clearly show an important trapping effect. But, the charging yield in MgO annealed at 1500 °C/4 h is almost zero whatever the crystallographic orientation. For our samples, since the contamination layer has been removed; the only possible traps are dislocations produced during polishing and eventually residual impurities. In the other hand, the annealing reduces the disorder dislocations network and minimises its density.[3] Thus, between the MgO annealed at 1500 °C/4 h and the as-received one, the dislocation networks is completely reduced in disorder and density. Trapping yield is hence zero because the majority of defects are restored and cured after annealing. At 1500 °C our samples tend towards pure MgO single crystal where no trapping can occur. This confirms results found by Vallayer et al.[8] This analysis is consistent with the reduction, with annealing, of the density and disorder of dislocations network.[4]

The MgO annealed at 1000 °C/2 h and the as-received one clearly show an significant trapping effect. We see that the trapping quickly decreases versus the quantity of injected charge because the trapped charges create a high electric field which acts against the trapping and increases the secondary emission. The same behaviour has been observed in sapphire implanted with zirconium ions.[9] We can see also that the MgO annealed at 1000 °C/2 h clearly shows a small increase in charge trapping compare to the as-received one. In the frame of the previous model, this fact must include the density of dislocations and the degree of the disorder of dislocations network, which offers mobility to trapped charges and decreases trapping ability. According to this model, impurity bands must be more broadened in the MgO as received than in the MgO annealed at 1000 °C. Thus, the density and the disorder of dislocation networks in the MgO as received must be more important than in the MgO annealed at 1000 °C.

4.2. Trapping ability and charge extension studies as function of crystallographic orientation

The defect effects on trapping properties is studied after heating at 1000 °C/2 h as function of crystallographic orientations. The two sample sets are treated in the same way as indicated in protocol above. The study of charging ability and charge extension is based on the analysis of both curves obtained by the two experimental methods. It was shown[10] that the trapping ability must be studied with low value of injection charge Q_i to avoid the charging effects due to the important quantity of trapped electrons. In Fig. 4 we have reported a mirror curve obtained after injection

charge of 100 pC for each crystallographic direction. Absorbed current curves recorded during this injection are reported in Fig. 5.

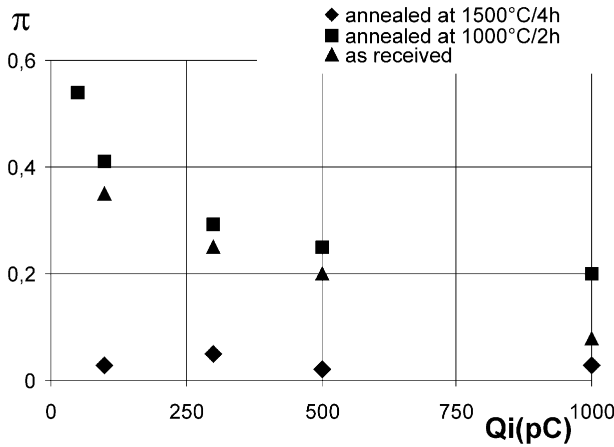

Fig. 3. Trapping yield of as-received MgO after annealing at 1000 °C/2 h and at 1500 °C/4 h for [100] crystallographic direction.

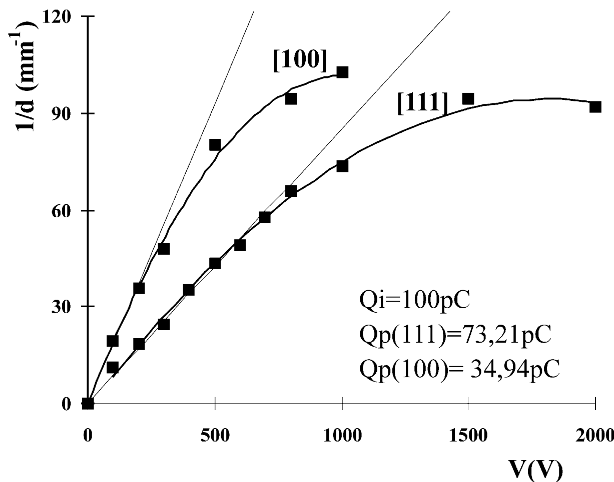

Fig. 4. Mirror curves as a function of crystallographic directions after annealing at 1000 °C/2 h.

It is observed that trapping depends on the crystallographic orientation . However, it is to be noted that the trapping is achieved through the charges induced by electron-holes pairs in the bulk. Consequently, it will not be influenced by the orientation of the incident beam. The difference in Fig. 4 can be interpreted as an effect of the superficial layer rich in dislocation which depend on the crystallographic orientation.[14]

It is known that slope of $\frac{1}{d}(V)$ curve obtained by mirror method is inversely proportional to charge trapping quantity Q_p[8] and that initial absorbed current I_{max} given by the absorbed current curve represents trapping ability of samples.[10] Fig. 4 shows that the slope of $\frac{1}{d}(V)$ curve in the [111] direction is lower than that of [100], and Fig. 5 shows that I_{max} for [111] direction is higher than that of [100]. These two facts show that charging is higher in the sample oriented (111) than in the sample oriented (100). According to the previous model, impurity bands must be more broadened in the (100) face than in the (111) face. Thus, the disorder of dislocations network in the (100) face must be more important than in the (111) face.

It is also known that bending in mirror plot means that the charge admits certain extension,[8] and that the decreasing way of absorbed current is linked to charge trapping density[10] as we have seen previously. Fig. 4 shows that bending in the (100) face is more precocious and charges are less stable than in the (111) plan, and, parallel, Fig. 5 shows that the average slope of absorbed current decreasing is equal to 2.67 nA s^{-1} and to 1.57 nA s^{-1} for, respectively, (111) and (100) faces; both results suggest that charge distribution in the (111) face is less expanded than in the (100) face. This analysis shows that dislocations network in the (111) face is more ordered than in the (100) face.

Finally, the sections are well consistent and lead us to conclude that the electron mobility in the (100) face is more important, because the subsurface mesostructure dislocations network is more disordered, than in the (111) face; depends on crystallographic orientations.

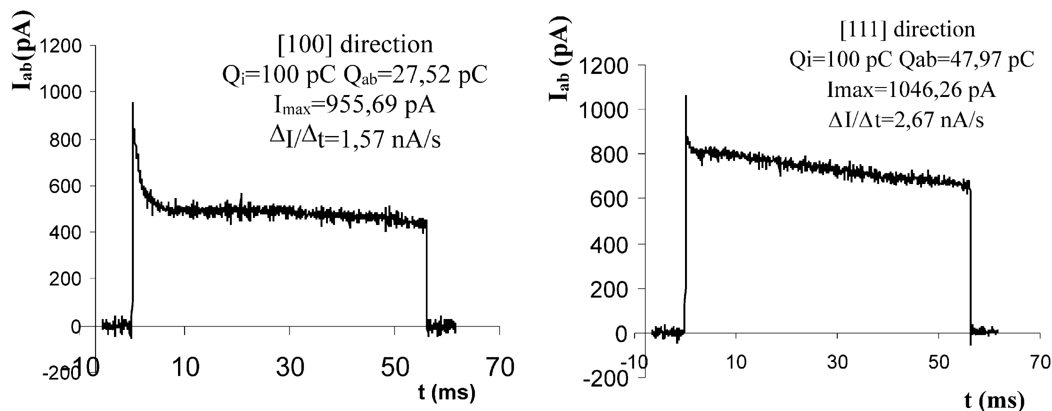

Fig. 5. Absorbed current for different crystallographic directions after annealing at 1000 °C/2 h.

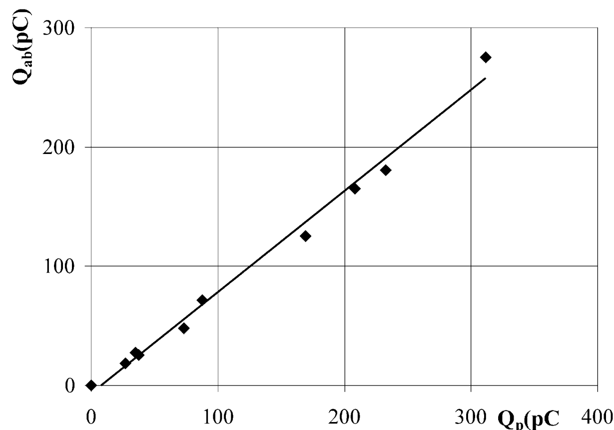

Fig. 6. Variation of Q_{ab} versus Q_p after annealing at 1000 °C/2 h.

4.3. Comparison between trapped charge and influence charge

It is important to compare trapped charge Q_p and influence charge Q_{ab} measured respectively by the mirror method and the absorbed current method. The variation of influence charge quantity versus the trapped charge is given in Fig. 6. We see clearly that the quantity of influence charge is proportional to the trapped one, according to Eq. (7). Vallayer[11] has shown that the proportionality coefficient is equal to 0.85 (for LEO 440 SEM). Compared to the fitting one (0.849) there is a good agreement between the two values.

5. Conclusion

The two complementary techniques: mirror method and absorbed current method are shown as powerful techniques for the study of charging properties of ceramics. Because trapping in pure MgO single crystal essentially occurs along dislocations, we have outlined the major polishing effect in trapping properties in MgO. A mesoscopic analysis (dislocation structure, etc.) is needed to explain the trapping phenomena. Based on the model of impurity band extended by Anderson states, we have analysed trapping and diffusion of charges in MgO. We have then shown the strong dependence of the charging ability due to the dislocation network which depends on annealing temperatures and crystallographic orientations.

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