EXPERIMENTS ON PHOTOEMISSION FROM FERROELECTRIC CERAMICS

I. Boscolo, S. Cialdi, M. Valentini, University and INFN, Via Celoria 16, 20133 Milano, Italy
L. Catani, F. Tazzioli, INFN-LNF, Via E. Fermi, 00044 Frascati - Roma, Italy
L. Giannessi, M. Quattromini, ENEA-CRE, Via E. Fermi, 00044 Frascati - Roma, Italy

Abstract

Photoemission yield of lead zirconate titanate lanthanum doped ceramic disks, illuminated with 532 and 355 nm radiation, in different experimental configurations is investigated. A new physical model is used to interpret the different behaviours.

1 INTRODUCTION

Lead zirconate titanate lanthanum doped, PLZT, ferroelectric ceramics showed interesting quantum efficiency and high non-linearity when illuminated with light ranging from green to UV [1, 2, 3]. The photoemission behaviour depends on prepoling [4] and polarisation [5] of the sample.

We have investigated photoemission from PLZT 8/65/35 (the first number refers to the atomic percentage of lanthanum with respect to lead and the other two numbers refer to the relative percentage of zirconium and titanium) illuminated with 532 ($2.32\,eV$) and $355\,nm$ ($3.5\,eV$) radiation. Our ceramics have a high defects density of both n and p type, hence they have the thermodynamical behaviour of relaxor ferroelectrics [6].

During the prepoling process [4] a fraction of defects moves to the two surfaces: n-type defects are accumulated at the negative side of the polarising voltage and p-type defects at the other side. The emitting surface can be made either of n-type or of p-type, depending on the direction of the electric field during the prepoling process.

The second and third harmonics of a Nd:YAG laser are used because the material has an energy gap of $3.3\,eV$, hence their absorption is much different [7]. In agreement with what expected, we have measured a 3-photon absorption process at $\lambda = 532\,nm$ and a 2-photon process at $\lambda = 335\,nm$.

2 EXPERIMENTAL SETUP

The experimental setup is discussed in a previous paper [3]. The anode-to-cathode distance is $3\,mm$. The charge is collected in a coaxial copper anode (Faraday cup) matched to a $50\,\Omega$ cable. The working pressure is maintained at approximately $\sim 3 \times 10^{-5}\,mbar$. The accelerating voltage was $5\,kV$.

The cathodes are disks of $16\,mm$ diameter, $0.7 - 1\,mm$ thickness, coated with a solid metallic film on the rear surface and with a grating interconnected by an external ring on the emitting surface. The two electrodes are used to set the polarising field through the sample. In the positive bias configuration a positive polarity is applied to the emitting surface electrode (i.e. the front electrode is positive with respect to the rear electrode) and the polarisation vector of the sample is oriented towards the rear surface. The polarising field applied to the samples was only $0.8\,kV/mm$. The electric field applied through the sample is segregated under the metallic stripes because of the high value (> 1000) of the dielectric constant ϵ. The cathode-anode accelerating field does not penetrate into the material because of the shielding effect of the front grid.

The ceramic slug is grown with the usual procedure [7].The slug is then cut in disks, which, after a polishing and cleaning treatment, are covered with electrode. The front grating has a period of $200\,\mu m$.

We have prepoled our samples so as to create an n-type region in the emitting surface layer. During the prepoling process O^{2-} vacancies (n-type) move towards the emitting surface and concentrate under the metallic stripes, while Pb^{2+} vacancies (p-type) move towards the rear elctrode. The defect concentration under the metal stripes, measured via thermo-stimulated charge measurements [8], was about $0.5\,\mu C/cm^2$.

3 EXPERIMENTAL RESULTS AND DISCUSSION

The electron emissions from prepoled samples illuminated at 532 and $355\,nm$ is shown in Fig. 1 in case of positive and negative polarisation. Measurements at $\lambda = 532\,nm$ have been performed with laser energies up to $800\,\mu J$. In case of $355\,nm$ radiation, the maximum laser energy was limited to about $250\,\mu J$ by the harmonic conversion process. The samples show a clear different behaviour at the two wavelengths: at the same laser energy the emission yield at $\lambda = 355\,nm$ is one order of magnitude larger than at $\lambda = 532\,nm$.

Our emission model is shown in Fig. 2. Oxygen vacancies (donor defects) are concentrated under the metal stripes; the polarisation (due to the applied bias) with its strong electric field pushes the electrons of these donor

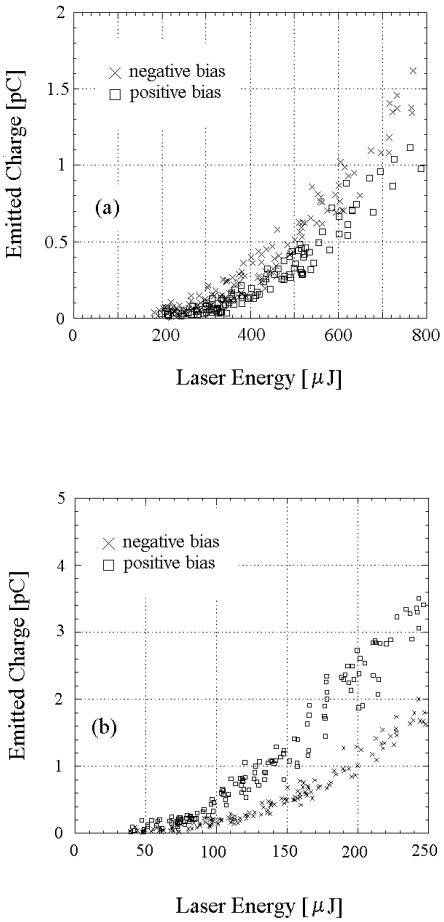

Figure 1: Emitted charge from a prepoled sample with positive (□) and negative bias (×): (a) with $\lambda = 532\,nm$ and (b) with $\lambda = 350\,nm$.

defects just against the surface. These electrons partially diffuse at the p-n junction created at the border of the stripe and drop into the p trap band; as a result the density of the initial states for photo-excitation is enhanced. The classical calculation of the diffusion leads to a diffusion layer of about $100\,nm$ with an electron density of about $10^{17}\,cm^{-3}$. The effect is further enhanced in positively-prepoled biased samples, it is instead reduced in negatively-prepoled biased samples.

The different behaviour at the two wavelengths is explained by the fact that the violet light is well absorbed within the $100\,nm$ electron rich surface layer, while the green light penetrates deeper into the material.

Arguing that the polarising electric field is segregated by the metallic stripes of the grid, a border effect was expected. For this reason, the emissions from $200\,\mu m$ and $100\,\mu m$ period grating are compared in Fig. 3. The bare surface available for the emission is the same in both cases, but the number of borders per unit area is a factor two higher in the case of $100\,\mu m$ period grid. The emission yield of the sample with more borders is about a factor two higher

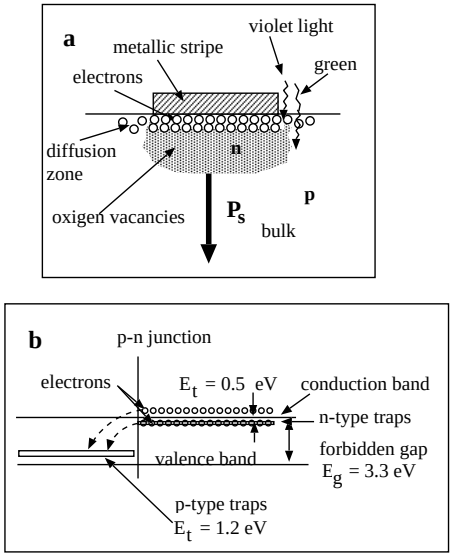

Figure 2: (a) Scheme of defect and electron density at the surface due to prepoling, polarisation and diffusion. (b) Energy band scheme at the junction created by the accumulation and depletion of donors respectively under the metallic stripe and outside. The broken arrows show the diffusion of electrons through the junction and their falling into the p band. The violet light is absorbed within the thin diffusion zone, the green light overcomes that layer.

with violet light and it does not change with green light. In fact, the border effect is effective with violet light because of the $100\,nm$ penetration length and it is not effective for green light because of the longer penetration length.

The emission measurements from un-prepoled samples show that the polarisation does not affect the photoemission in this case. This result is in agreement with the proposed model.

We have also performed tests with samples with reversed prepoling: the emission was considerably lower than in the above-mentioned cases and it was not influenced by the bias.

The action of a polarising bias is explained by the high electric field created in the surface layer. The ceramics surfaces have different properties than the bulk [5, 11, 12]. The surface layer of a thickness estimated around $20\,nm$ is not in ferroelectric phase (also because of the defect excess), hence the dielectric constant of the surface layer is much lower than that of the bulk. Its value can be roughly assumed around 10 against a value of more than 1000 for the bulk. Because of this, a large electric field is established in the surface layer.

4 CONCLUSIONS.

The highest electron emission yield has been obtained by prepoling the sample with negative voltage at the front grid and by applying a positive bias on the same side. Prepoling and polarisation have a significant influence on the emis-

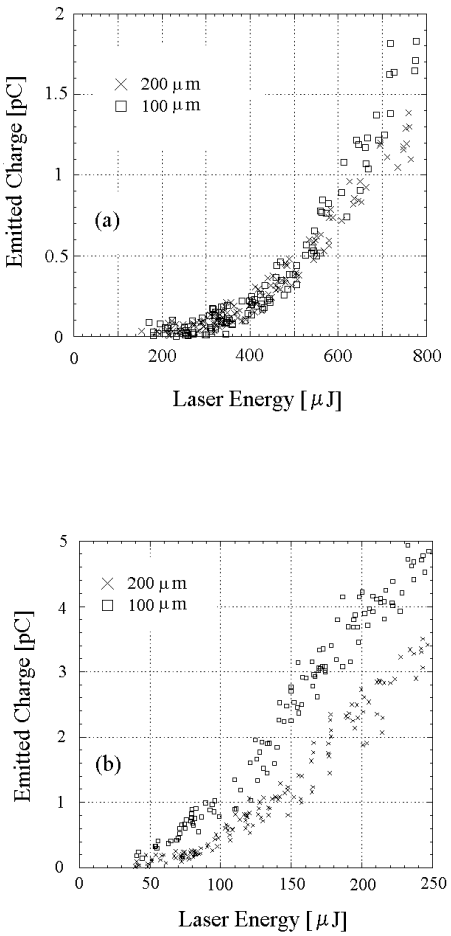

Figure 3: Comparison of the emissions of two prepoled and negatively polarised samples with a $100\,\mu m$ (□) and $200\,\mu m$ (×) grid period: (a) with $\lambda = 532\,nm$ and (b) with $\lambda = 350\,nm$.

sion properties.

The atomic scale model outlined in the paper for explaining the photo-emission properties of the ceramics is able to enlighten the relation between the experimental observations and the material properties.

The measured quantum efficiency, larger than $3 \cdot 10^{-7}$ at a relatively low radiation intensity, indicates that these ceramics are promising candidates as photoemitters, especially considering that the emission seems to be confined at the borders of the grid stripes.

5 REFERENCES

[1] K. Geissler, H. Gundel, H. Riege, J. Handerek, Appl.Phys. Lett. 56, 895, 1990.

[2] G. Benedek, I. Boscolo, Appl. Phys. Lett. 72, 522, 1998.

[3] I.Boscolo et al. Applied Physics Letters, 74, 859, 1998.

[4] H. Gundel, J. Handerek, H. Riege, E.J.N. Wilson and K. Zioutas, Ferroelectrics 100,1,1989.

[5] M. E. Lines and A.M. Glass, “Principles and Applications of Ferroelectric and Related Materials”, Clarendon Press, Pxford, 1977.

[6] Q.Y. Jiang, E.C. Subbarao, Cross, J. Appl. Phys. 75, 7433, 1994.

[7] S. H. Hartling, “Ceramic Material for Electronics”, ed R. C. Buchanan, Marcel Dekker Inc. 1991, pag 129.

[8] J. Handerek, Z. Ujma, J. Phys. Condens. Matter 7, 1721, 1995.

[9] G. Smolenski, A. Agranovskaya, Sov. Phys. Solid State, 1, 1429, 1960; 2,2584,1986.

[10] L. Eric Cross, Ferroelectrics, 76, 241, 1987.

[11] K.Szot, W.Speier, S. Cramm, J.Herion, Ch. Freiburg, R.Waser, M.Pawelczyk, W.Eberhart, J. Phys. Chem. Solids, 57, 1765, 1996.

[12] S.Miga, K.Szot, Ferroelectrics, 1994, vol. 160, pp. 137-144.