Investigation of irradiated ferroelectric thin films

R. Bittner 1), K. Humer 1), H. W. Weber 1), M. Tyunina 2,3), L. Cakare 4,2), A. Sternberg 2)

1) Atomic Institute of the Austrian Universities, A-1020, Vienna, Austria
2) Institute of Solid State Physics, University of Latvia, Riga, Latvia
3) Microelectronics Laboratory and EMPART Research Group of Infotech Oulu,
University of Oulu, Finland
4) Jozef Stefan Institute, Ljubljana, Slovenia

e-mail contact of main author: Roland.Bittner@ati.ac.at

Abstract. Irradiation effects on highly oriented $Pb_1Zr_{0.53}Ti_{0.47}O_3$ (PZT), $Pb_{0.94}La_{0.06}Zr_{0.65}Ti_{0.35}O_3$ (PLZT-6), and $Pb_1Zr_1O_3$ (PZ) ferroelectric (FE) and antiferroelectric (AF) thin films are investigated with respect to their possible application as a temperature sensitive element in a new bolometer system for ITER. The PZT and PZ films were deposited by a sol-gel technique on a $Pt/TiO_2/Si$ substrate, whereas the PLZT-6 film was deposited by pulsed laser deposition (PLD) on a LSCO/MgO (100) substrate. The dielectric properties, i.e. the hysteresis loop and the dielectric constant of the films, were investigated in a frequency range from 20 Hz to 100 kHz and at temperatures up to 300 °C, before and after neutron irradiation to a fast neutron fluence of $5x10^{21}$ m^{-2} (E > 0.1 MeV). The dielectric constant was measured during cooling with 2 $°C.min^{-1}$. The dielectric properties of the films were measured before and after annealing to 300 °C.

1. Introduction

Ferroelectrics are known to be radiation hard materials with good dielectric properties. Therefore, Di Maio [1] suggested to employ them as an alternative bolometer system for ITER in a device based on resonance frequency measurements of an electric resonant circuit. The ferroelectric thin film plays the role of a dielectric in a capacitor. Due to radiation induced heating of the capacitor, the ferroelectric film alters its dielectric constant following the Curie Weiss law in the paraelectric regime. This leads to a change in the resonance frequency of the circuit. Such a bolometer is less sensitive to electromagnetic noise and requires only one transmission line for several channels, which is important for remote handling. The ferroelectrics are used in the paraelectric regime. The operating temperature must be in a range above the Curie temperature (T_c), but not too close to it, because the ferroelectric material is most sensitive to neutron irradiation [2] near T_c. Unfortunately, most of the irradiation results are related to ceramics, and only a few to neutron irradiation. We present studies of the influence of neutron irradiation on the dielectric properties of FE thin films, i.e. their dielectric constant and the hysteresis loops.

2. Experimental

The PZT film (thickness 1.08 µm) and the PZ film (thickness 0.9 µm) were deposited by a sol-gel technique [3] (spin coating process) on a $Pt/TiO_2/Si$ substrate, using lead oxide as a precursor material, which leads to improved properties. The PLZT-6 film [4] with a thickness of 250 nm was deposited by pulsed laser deposition (PLD), using a XeCl excimer laser, on a LSCO/MgO (100) oriented substrate. All films are perovskites (ABO_3 structure).
Spring contacts, instead of silver contacts, were used to avoid an activation of the contacts during irradiation.

The dielectric properties of the films were investigated in a frequency range from 20 Hz to 100 kHz and at temperatures up to 300 °C, before and after neutron irradiation to a fast neutron fluence of 5×10^{21} m $^{-2}$ (E > 0.1 MeV) in the TRIGA Mark II reactor, Vienna. The dielectric constant was measured during cooling with a cooling rate of 2 °C.min^{-1}. The frequency dependence of the dielectric constant was measured with a 5210 lock-in amplifier, and the hysteresis curves with an RT6000 HVS testing system. The temperature variation was achieved by a programmable heating plate.

3. Results

Figure 1 shows the hysteresis loops of the films before (full symbols) and after (open symbols) neutron irradiation. The PZ film shows a typical AF behaviour, where the remanent polarisation P_r is very small at zero voltage (in the ideal case $P_r = 0$). The PLZT-6 and PZT film show FE behaviour, but the loop of the PZT film is distorted, which could be related to secondary phases (non-ferroelectric phases).

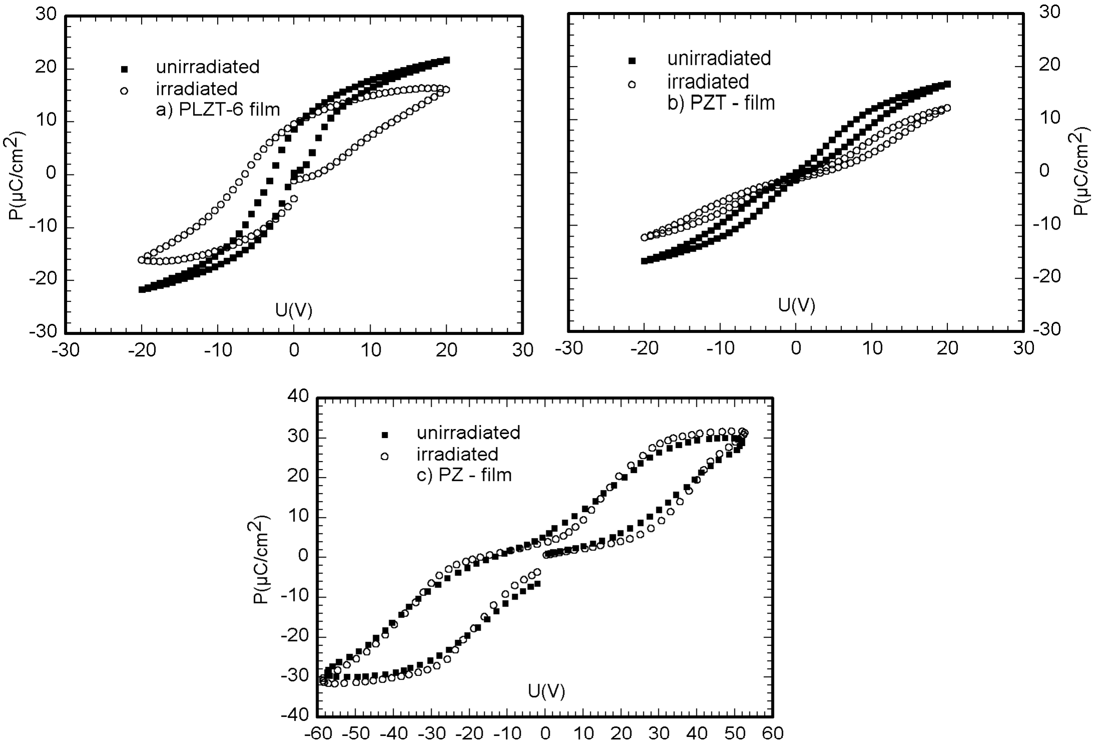

Fig. 1. Hysteresis loops for (a) PLZT-6-, (b) PZT –, (c) PZ - films measured at 20 Hz and at room temperature before and after irradiation. The contact areas are 0.2 mm^2 (a), 0.3 mm^2 (b), and 1.0 mm^2 (c).

After neutron irradiation, the behaviour of the FE and the AF films is different. In both FE films, a clear reduction of the maximum polarisation can be observed, but no significant differences were found in the PZ film. In this film only the AF behaviour was enhanced. A similar effect of x-ray irradiation was reported for FE multidomain triglicyne sulfate [5]. The radiation induced electron-hole pairs are separated by the internal electric field of the polarised domains, which depolarises the domains. This effect leads to an AF shape of the hysteresis loop in multidomain materials.

The hysteresis curve of PLZT-6 (open symbols) is wider, indicating that more energy is needed to switch the polarised domains into the opposite direction (“frozen domains”).

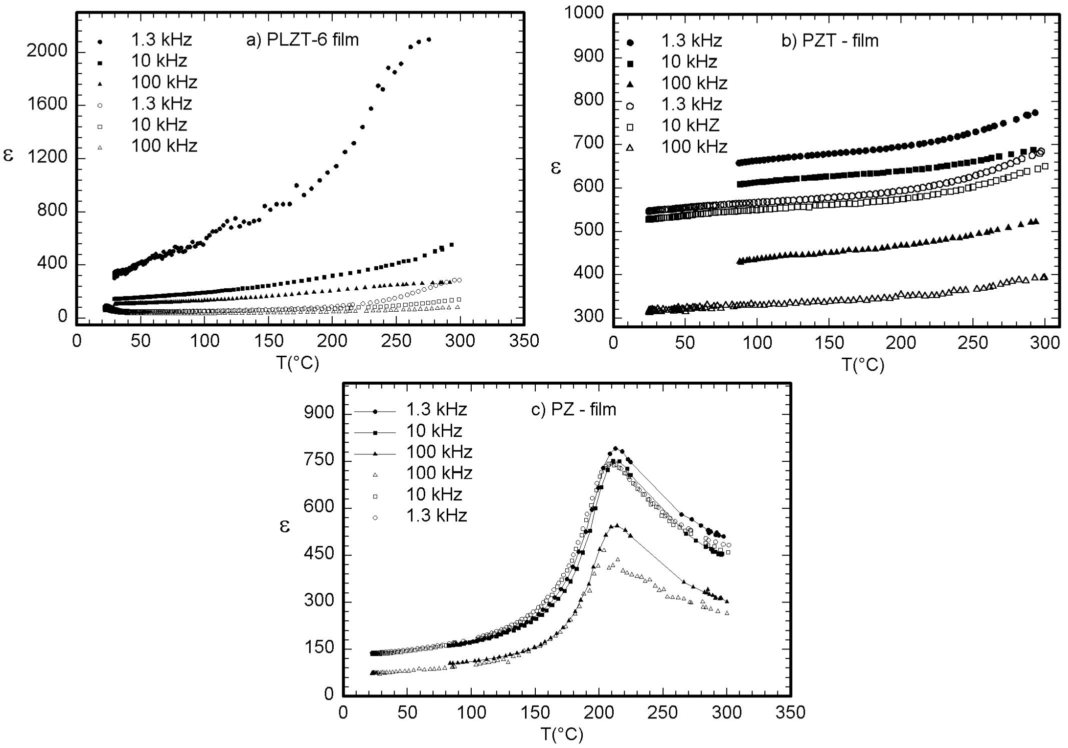

Fig. 2. Frequency dependence of the dielectric constant as a function of temperature, before (full symbols) and after irradiation (open symbols).

Figure 2 shows the dielectric constant of the films. The PLZT-6 film *(FIG. 2a)* does not show the peak around 200 °C expected from work on ceramic PLZT-6 samples [2]. Instead, we observe a considerable increase of the dielectric constant above ≈150 °C, which could be expected from the analysis of thin FE films in the frame of the Ising model [6]. This “second” peak could mask the expected peak at the Curie point of bulk ceramics. We also notice, that the dielectric constant is extremely reduced after neutron irradiation (open symbols in *FIG. 2a*), in contrast to the other films (see *FIG. 2b and 2c*). On the other hand, the PZ - film *(FIG. 2c)* does not show significant changes between the irradiated (open symbols) and the unirradiated (full symbols) state. Only the maxima of the dielectric constant are lower and the phase transition temperature is shifted from 220 °C to 210 °C, as expected from literature [2]. For the PZT – film we do not observe a peak, as expected, because the phase transition temperature is outside our measuring range. However, the reduction of the dielectric constant after irradiation is pronounced.

4. Conclusion

We measured the dielectric properties of a PZT- and a PLZT-6 - film, which are ferroelectric materials, and of a PZ – film, which is an antiferroelectric material, with respect to their possible application as a temperature sensitive element in a new bolometer system for ITER. The investigations are made in the temperature range from 20 to 300 °C and in a frequency range from 20 Hz to 100 kHz. The hysteresis loop and the dielectric constant were measured before and after fast neutron irradiation to $5x10^{21}$ m^{-2}. We find that neutron irradiation reduces the maximum polarisation of the hysteresis loops in the FE material and freezes the polarised domains in the PLZT-6 film. For the PZ – film, we find an enhancement of the AF behaviour after irradiation, but no reduction of the polarisation (P_{max}). All films show reduced dielectric constants, but the same general behaviour as before neutron irradiation. The observed irradiation effects may be caused by charges trapped at radiation induced defects (vacancies, Frenkel pairs, ...). This internal bias field splits and traps the polarised domains.

To systematically characterise these perovskites, more detailed investigations will be made. To identify the defects, caused by neutron irradiation, further annealing experiments are necessary (up to ≈500 °C). With respect to a possible application in fusion devices, investigations of additional materials, such as $Pb_1(Zr_{1-x}Ti_x)O_3$ (PZT), $(Pb_{1-x}La_x)(Zr_{1-y}Ti_y)O_3$ (PLZT), with different compositions (x, y), and irradiations to higher neutron fluences are necessary.

Acknowledgements

This work has been carried out within the association EURATOM – OEAW.

References

[1] M. Di Maio, PhD. Thesis, RWTH Aachen (1999)

[2] A. Sternberg, A. Spule, L. Shebanovs, E. Birks, H. W. Weber, H. Klima, F. Sauerzopf, Key Engineering Materials, **132-136** (1997), 1096 - 1099

[3] M. Kosec, U. Delalut, B. Malic, V. Bobnar, G. Drazic, ISAF´96: Proc. 10th Internat. Symp. on Applications of Ferroelectrics (IEEE Cat. N°96CH35948), 443 – 445

[4] M. Tyunina, J. Levoska, A. Sternberg, S. Leppavuori, J. Appl. Phys., **84** (1998), 6800 – 6809

[5] Jean-Luc-Leray, Olivier Musseau, Philippe Paillet, Jean-Luc Autran, J. Phys. III France **7** (1997), 1227

[6] B. Qu, W. Zhong, P. Zhang, Phys. Rev. B **52** (1995), 766