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# A study of electrical and optical fatigue in PMNT films on titanium nitride substrates

**A Fundora**[1], **E Martínez**[1,2] **and J M Siqueiros**[1]

[1] Centro de Ciencias de la Materia Condensada, Universidad Nacional Autónoma de México, Apartado Postal 2681, Ensenada, Baja California, 22800, Mexico
[2] Centro de Investigación en Materiales, DIP-CUCEI, Universidad de Guadalajara, Apartado Postal 2-638, CP 44281, Guadalajara, Jalisco, Mexico

E-mail: guerra@ccmc.unam.mx

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**Abstract**

$Pb(Mg_{1/3}Nb_{2/3})_{0.90}Ti_{0.10}O_3$ (10PMNT) polycrystalline thin films were deposited on TiN/Si substrates by laser ablation using 248 nm wavelength, 30 ns duration pulses from a KrF excimer laser with a 10 Hz repetition rate and a fluence of 2 J $cm^{-2}$. The samples were deposited at 250 °C and post-annealed at temperatures between 500 and 600 °C. The presence of a dominant 10PMNT perovskite phase was confirmed by x-ray diffraction analysis as well as a secondary pyrochlore phase whose relative abundance increased with the annealing temperature. The electrical properties and the influence of the annealing temperature on the dielectric properties of the 10PMNT thin films were characterized through $P$–$E$ hysteresis loop studies. Electrical and optical stress measurements were used to evaluate the long-term performance of the 10PMNT/TiN/Si heterostructure. We demonstrate that rejuvenation of electrically fatigued PMNT films is possible by applying optical stress via UV light; however, it can also be limited by other factors. We suggest that polarization fatigue in PMNT is essentially a dynamic competition between domain wall pinning due to electronic charge trapping and trapped charges like oxygen vacancies at the interface and UV/electric field-assisted unpinning of the domain wall.

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

$Pb(Mg_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ (PMNT), a well known relaxor ferroelectric, is one of the most promising ferroelectric materials due to its high dielectric constant, giant electromechanical response, large electro-optic coefficients, and excellent piezoelectric properties [1–8]. Recently, PMNT thin films have been of great interest for a variety of integrated device applications,

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such as in dynamic random access memories (DRAM), optical memories, pyroelectric devices, piezoelectric and electro-optic devices, etc [9–11]. PMNT thin films have been prepared using various techniques, such as sol–gel [12, 13], pulsed laser deposition [14, 15], metal–organic chemical vapour deposition [16, 19] and rf sputtering deposition techniques [17]. In order to integrate perovskite oxide films on Si substrates without inter-diffusion and reactions, an appropriate approach is the introduction of buffer layers which are lattice matched with both perovskite thin films and silicon, that can be grown at relatively low temperatures, and can act as diffusion barriers. TiN thin films have attracted much attention for their potential application as a chemically stable buffer layer on Si. Epitaxial or oriented TiN films are preferred for the deposition of ferroelectric thin films since epitaxial films demonstrate better properties than their polycrystalline counterparts [18]. Among the most important electrical properties of ferroelectric thin films for nonvolatile memory applications are those related to the electrical stability like ageing, fatigue, imprint and retention. Electrical fatigue, in particular, is a significant indicator of the reliability for ferroelectric random access memory (FRAM) devices that use a destructive readout operation, i.e., the switching of polarization for each read/write operation. Several phenomenological scenarios, as well as microscopic descriptions of the origin of fatigue, have been proposed [20–22]. Basically, all these models are dealing with the elements of the following two-step general scenario: (i) electrical stress results in a creation or redistribution of imperfections in the ferroelectric capacitor, and (ii) the imperfections influence the switchable polarization. These imperfections are related mainly to ionic defects such as oxygen vacancies typical of Pb based systems and electrons and holes injected from the electrode into the ferroelectric film. The most acceptable explanations for suppression of polarization are: (1) the bulk pinning of domain walls where the individual domains do not contain active centres of opposite domain nucleation, where the most probable driving force is the migration and trapping of free electrons and oxygen vacancies, (2) inhibition of the seeds of opposite domain nucleation at the interface and (3) formation of a passive surface layer that reduces the electric field seen by the ferroelectric film caused by the nearby electrode injection of electrons [23]. Switchable polarization can also be suppressed by optical stress (optical fatigue) when the material is illuminated with band gap light creating domain pinning electronic charge trapped at the domain boundaries [24]. A restoration of the polarization is possible if the trapped carriers recombine with opposite sign carriers releasing domains and allowing them to reorient, as has been suggested by other authors [23]. The main objective of this report is to demonstrate the electrical fatigue in PMNT films using titanium nitride as the bottom electrode. We demonstrate that rejuvenation of electrically fatigued PMNT films is possible by applying optical stress via UV light and assisted by an electric field; however it also can be limited by other factors.

## 2. Experimental details

The 10PMNT/TiN films were grown by pulsed laser deposition (PLD) in a high vacuum chamber with a base pressure of $10^{-4}$ Pa and a working oxygen pressure of 26 Pa. The target was fixed to a rotating mount moving at constant angular speed to favour thickness uniformity. A KrF excimer laser (LEXTRA 200 from Lambda Physik) with 248 nm wavelength, 30 ns pulse duration, 10 Hz repetition rate and a fluence of 2 J $cm^{-2}$ was used for deposition. The distance between the target and the TiN/$SiO_2$/Si (100) substrate was 100 mm. For the deposition, the TiN/Si substrate was initially heated up to 250 °C and maintained for a few tens of pulses with the purpose of providing the deposited material enough mobility to form a continuous layer. The heat supply was then turned off and the rest of the deposition was performed as the substrate cooled down to room temperature. The resulting films were annealed at 500,

**Table 1.** Electrical properties of the PLD deposited 10PMNT film on TiN substrates.

| 10PMNT | $P_r$ ($\mu$C cm$^{-2}$) | $E_c$ (kV cm$^{-1}$) |
|---|---|---|
| 500 °C | 6 | 35 |
| 600 °C | 8 | 65 |

550 and 600 °C (10PMNT500, 10PMNT550 and 10PMNT600) at ambient pressure for 15 s. The TiN films were prepared by using reactive sputtering of Ti in a 9 to 1 mixture of argon and nitrogen at a pressure of 0.6 Pa, with the substrate temperature of 450 °C. The resulting TiN films were polycrystalline according to x-ray diffraction measurements. Depth profiles of PMNT/TiN/$SiO_2$/Si films were performed in a scanning Auger microprobe (SAM) PHI-595 equipped with a differentially pumped $Ar^+$ ion gun. The polarization ($P$–$E$) measurements of the PMNT thin films were made at room temperature with an RT-66A ferroelectric tester from Radiant Technologies, Inc. Top electrodes of $RuO_2$ were evaporated using a stainless steel mask, producing capacitors with areas of $7 \times 10^{-4}$ cm$^2$ on PMNT films of 5000 Å thickness. The ferroelectric fatigue tests were performed using a 1 kHz, 5 V sinusoidal voltages. A 200 W Oriel Hg arc lamp ($\lambda = 365$ nm) was used to shine UV light on the 10PMNT thin films for charge photo-induction experiments.

## 3. Results and discussion

Figure 1 shows the XRD patterns for the 10PMNT thin film deposited at 250 °C by PLD and post-annealed at 500, 550 and 600 °C. A pure perovskite polycrystalline phase is observed in figure 1(a). Figures 1(b) and (c) show a multiple-phase polycrystalline growth where a residual pyrochlore phase is present and it grows as the annealing temperature increases. However, the perovskite phase is clearly the dominant crystalline phase. The reason for the pyrochlore formation as the temperature increases is that above 500 °C the solid solution becomes lead deficient due to Pb volatilization, allowing the formation of a $Pb_2Nb_2O_7$ pyrochlore phase. A deterioration of the dielectric properties of the film is to be expected for higher annealing temperatures.

The corresponding hysteresis loops for the 500 and 600 °C annealed films are presented in figure 2 and the measured values for $E_c$ and $P_r$, which are comparable to those reported by Maria *et al* [25], are presented in table 1. From the analysis of figure 2, it can be seen that the dielectric losses of the film annealed at 500 °C are smaller than those of the 600 °C film due to the presence of the pyrochlore phase at higher annealing temperatures. It is also a result of this measurement that the coercive field is almost twice as large in the 10PMNT600 film as in the 10PMNT500 film. Such behaviour suggests the existence of domain pinning space charge in the grain boundaries demanding a larger field for the domain switching process.

### *Electrical fatigue*

Figure 3 shows the hysteresis loops for the 10PMNT/TiN/$SiO_2$/Si (100) annealed at 500 and 550 °C before and after the fatigue process applying a 1 kHz periodic field at ±5 V for $10^6$ cycles. For 10PMNT500 films the lowering of polarization values is very probably related to the oxygen vacancies and free charge as they position themselves at the field-favourable regions of the domain walls weakening the polarization field. The values of the polarization change due to the accumulation of the space charge at the domain boundaries and of oxygen vacancies at the ferroelectric–electrode interface during the electrical fatigue test debilitating the polarization field and making it difficult for the domains to switch with the driving field.

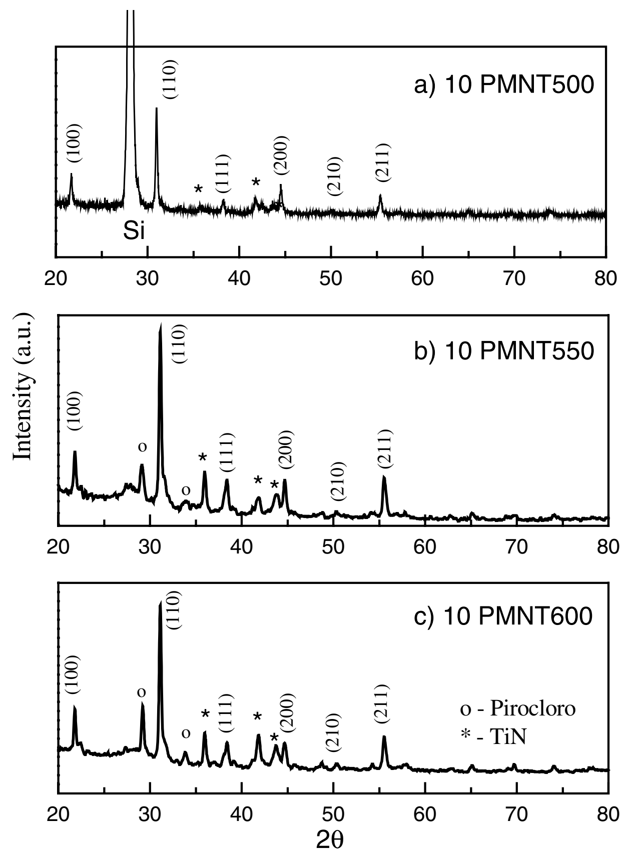


**Figure 1.** Diffraction patterns of 10PMNT thin film post-annealed at (a) 500 °C, (b) 550 °C and (c) 600 °C. Only the 500 °C is completely pyrochlore free.

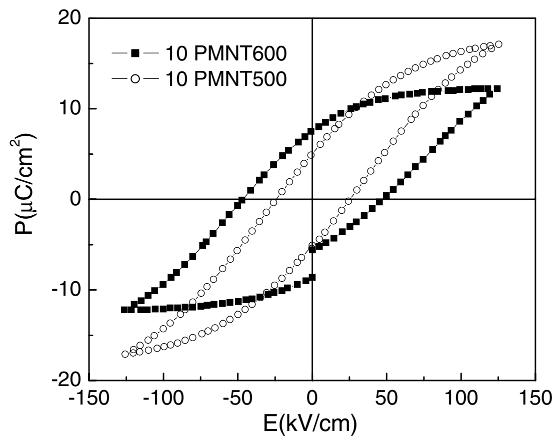


**Figure 2.** Ferroelectric hysteresis of the 10PMNT500 and 10PMNT600 samples as indicated. $P_r$, $P_{max}$ and $E_c$ are smaller in the sample annealed at 500 °C.

A similar behaviour is observed in 10PMNT films annealed at 550 °C (figure 3(b)) and 600 °C (figure 4) (10PMNT600). The reduction of the polarization in 10PMNT600 films is

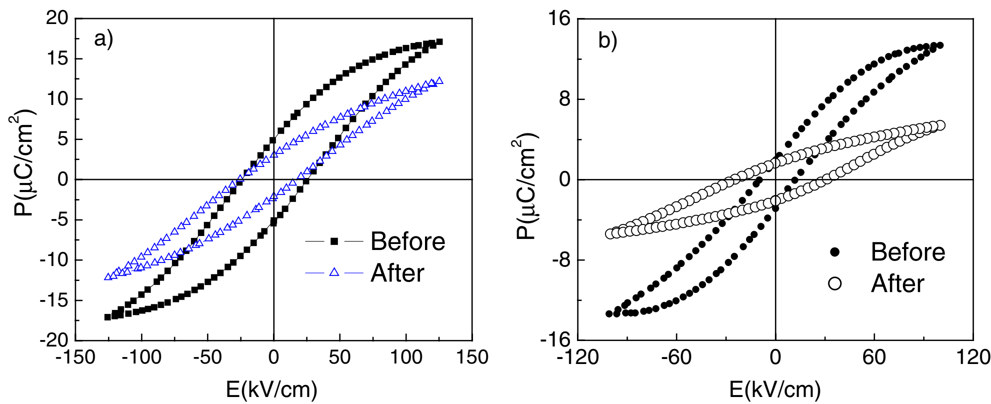


**Figure 3.** Ferroelectric hysteresis before and after electrical fatigue for the (a) 10PMNT500 and (b) 10PMNT550 samples at 5 V. For electrical fatigue the field switches at 1 kHz between ±5 V for $10^6$ cycles.

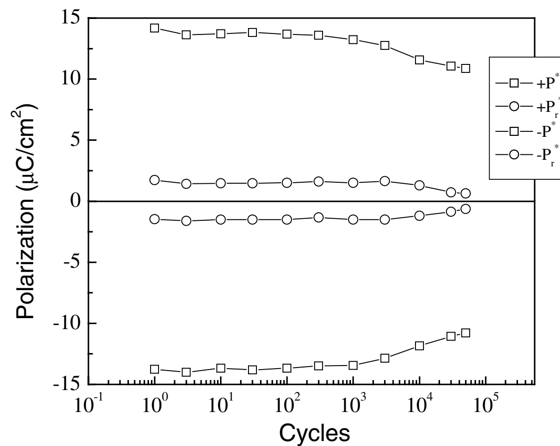


**Figure 4.** Electrical fatigue tests performed on 10PMNT600 films applying ±5 V for $10^5$ cycles.

due to the presence of the residual phase pyrochlore, a phase of much lower permittivity, that favours the accumulation charge at the domain boundaries which drives the domain pinning. Figure 4 shows the degradation of the polarization in terms of the behaviour of different polarization parameters ($+P^*$, $+P_r^*$, $-P^*$, $-P_r^*$) versus the number of fatigue cycles for the 10PMNT/TiN film annealed at 600 °C for $10^5$ cycles, under the above-mentioned conditions. $+P^*$ is related to polarization that comes from an inversion processes at the maximum positive applied electric field. $+P_r^*$ is the remanent polarization that comes from a positive voltage from an inversion process. $-P^*$, $-P_r^*$ are defined in a similar way but for negative voltages. The relaxation of the polarization is evident, further supporting the assumption that domain switching is being hindered by space charge and other defects causing a decrease in the remanent polarization.

To study the oxygen distribution from the surface to the substrate and to have a better argument about the presence of oxygen vacancies at the interfacial region an Auger depth profile analysis was done for the 10PMNT600 samples. A concentration profile against sputtering time of the sample component elements obtained in real time is presented in figure 5.

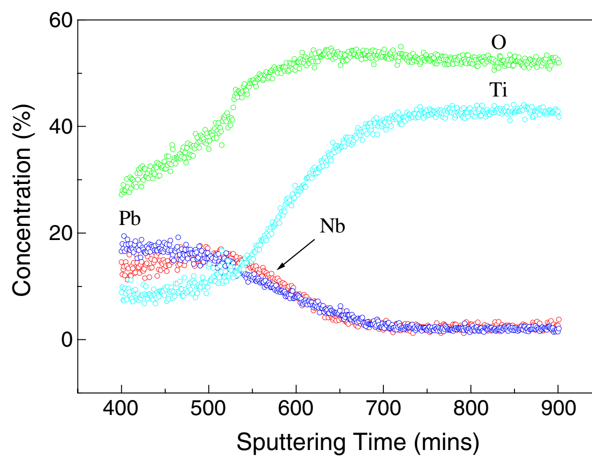


**Figure 5.** Concentration profile of the component elements of the PMNT600/TiN/Si thin films obtained by Auger electron spectroscopy.

From the figure it is possible to observe an oxygen gradient where it increases through the inside of PMNT film making the surface layers deficient in oxygen, supporting our theory of electrical fatigue assisted by this interfacial condition. The oxygen vacancies act as trapped charges which pin dipoles near to the interface to the electrode. Besides the action of oxygen vacancies we must consider the electrons and holes injected from the electrode or created during the fatigue test. As additional information to be considered, an inhomogeneous interface and the oxidation of the titanium nitride were observed.

*Optical fatigue*

In order to analyse the effect of optical stress on the electrically fatigued PMNT films we illuminated samples with UV light in combination with an electric field of +5 V. In figure 6(A), the $P$–$V$ behaviour before and after the electrical fatigue is shown. After electrically fatiguing the sample, a regenerating treatment with UV light/+5 V was applied and the effect is presented in the same graph. A restoration of the original behaviour is evident after the optical treatment and is explained by the presence of the photo-generated carriers. The rejuvenation process takes place because the photo-generated charge carriers (electrons and holes), being effectively redistributed by the electric bias field, lower the electrostatic barrier for domain reorientation by effectively reducing the space charge at the domain boundaries. The net result is that light promotes domain reorientation in fatigued films as suggested by some authors [26, 27]. On the basis of these results we suggest that electrical fatigue is a dynamic competition between domain wall pinning due to the electronic charge trapping and UV/electric field-assisted unpinning of the domain wall. The unpinning processes might include (a) overcoming of the pinning forces by the cycling field, (b) field-assisted detrapping of trapped carriers and (c) recombination of photo-generated with trapped charge, which can also lead to domain wall unpinning.

However, in figure 6(B) corresponding to 10PMNT600, a catastrophic effect on the polar behaviour of the sample is observed after the UV/+5 V treatment. A greater Pb loss is expected when the samples are heat treated at higher temperatures leading to larger numbers of oxygen vacancies as is shown from the AES spectrum (figure 5). When the UV/+5 V treatment is applied to the samples, the rejuvenation process does not take, due possibly to the higher space charge density besides occupation of deepest levels making ineffective the recombination

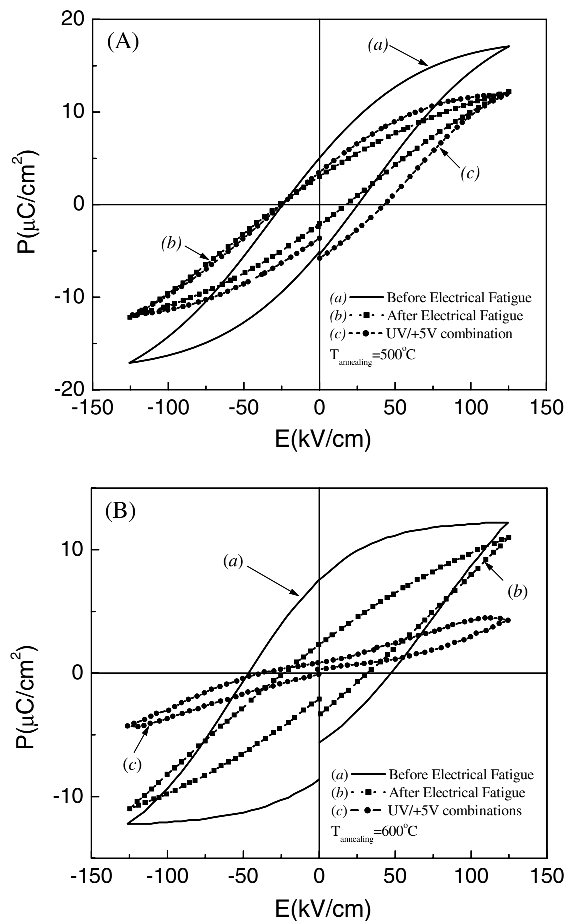


**Figure 6.** Hysteresis loops of (A) $RuO_2$/10PMNT500/TiN and (B) $RuO_2$/10PMNT600/TiN capacitors, for (a) before optical illumination, (b) after $1 \times 10^6$ bipolar switching cycle electrical fatigue and (c) after +5 V/light combination for 35 s.

process with the photo-generated carriers. The electrical and optical stress favours a spatial charge redistribution causing domain pinning. It leads to an enhanced depolarizing field that minimizes the polar behaviour of the samples. The pinning and unpinning processes can be influenced by at least four factors: (a) availability of electronic charge carriers, (b) the magnitude of the ferroelectric polarization, (c) concentration and mobility of oxygen vacancies and (d) the nature and concentration of the trapping centres present in the material. These four factors have to be taken into account to explain the effect of the photo-induced changes in the electric fatigue behaviour of 10PMNT films processed at different annealing temperatures.

## 4. Conclusions

$Pb(Mg_{1/3}Nb_{2/3})_{0.90}Ti_{0.10}O_3$ films were deposited on TiN. The samples were annealed at 500, 550 and 600 °C. The film annealed at 500 °C consisted of a single perovskite phase whereas the films heat treated at 550 and 600 °C showed a pyrochlore residual phase that becomes more abundant as the annealing temperature is raised. The remanent polarization, saturation

and coercive field values from thin film annealing at 500 °C are comparable to those reported previously [25]. From the fatigue measurements performed on the $Pb(Mg_{1/3}Nb_{2/3})_{0.90}Ti_{0.10}O_3$ on TiN films, annealed at 500, 550 and 600 °C, it was observed that in the 550 and 600 °C films a deterioration of the remanent polarization started after only $10^3$ inversion cycles. The fatigue process is attributed to free charge at the domain boundaries, oxygen vacancies at the electrode–ferroelectric film interface and the presence of a residual pyrochlore phase.

It is an interesting result that the best structural and dielectric properties were obtained at the lowest annealing temperature and that the complete sample preparation process does not involve temperatures above 500 °C opening the possibility for integration with silicon technology of the $Pb(Mg_{1/3}Nb_{2/3})_{0.90}Ti_{0.10}O_3$ ceramic. For the moment, the fact that fatigue appears at a relatively low number of inversion cycles ($10^3$–$10^4$) precludes the use of this ferroelectric–electrode system where polarization inversion is required for long periods of time. Better stoichiometry control and an optimization of the ferroelectric–electrode performance are still open problems to solve for this material.

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