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The effects of irradiation by X rays and protons on the dielectric and piezoelectric response of highly (100)-textured polycrystalline $Pb(Zr_xTi_{1-x})O_3$ (PZT) thin films have been studied. Low-field dielectric permittivity, remanent polarization, and piezoelectric $d_{33,f}$ response all degraded with exposure to radiation, for doses higher than 300 krad. At first approximation, the degradation increased at higher radiation doses, and was stronger in samples exposed to X rays, compared to the proton-irradiated ones. Nonlinear and high-field dielectric characterization suggest a radiation-induced reduction of the extrinsic contributions to the response, attributed to increased pinning of the domain walls by the radiation-induced point defects. © *2013 AIP Publishing LLC*.
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Ferroelectric thin films with large dielectric permittivity, piezoelectric coefficients, and electromechanical coupling are attractive for a range of applications such as random access memories, multilayer capacitors, energy harvesting devices, micro- and nano-electromechanical sensors and actuators, and micro-scale mechanical relays.[1,2] Especially of interest are autonomous microsystems for use in locations with limited access or in harmful conditions. Among such applications, use of devices in locations with exposure to radiation is of particular interest, specifically where the radiation dosage might be harmful to humans. For devices operating in locations with high radiation exposure (nuclear power plants, space applications, etc.), it is imperative to characterize the response of the active (ferroelectric) material as a function of radiation dose in order to assess the device behavior and functionality in the same conditions.

Previous studies of effects of ionizing radiation on properties of ferroelectric thin films have been mostly limited to the polarization retention properties of $Pb(Zr_xTi_{1-x})O_3$ (PZT) thin films with their application to memory devices as the primary objective.[3–5] The observed reduction in the remnant polarization has been attributed to increased space-charge regions near the electrodes, by trapping of radiation-induced charges in the ferroelectric material[6] (often identified as oxygen deficiencies).[3,5] However, with the growing interest in ferroelectric films for piezoelectric microelectro-mechanical systems (MEMS), knowledge of the effects of irradiation on a wider range of materials' properties, including electromechanical response becomes of the paramount importance. Here, we investigate variations of the low- and high-field dielectric and effective piezoelectric response of highly (100)-textured PZT thin films as a function of irradiation by X rays and protons, for doses up to 2 Mrad.

PZT thin films were deposited on platinized Si substrates via chemical solution deposition.[7,8] A chemical precursor solution of PZT with nominal composition of $Pb_{1.2}(Zr_{0.53}Ti_{0.47})O_3$ was prepared based on a 2methoxyethanol (2MOE)-route.[9] The solution was adjusted at 0.4 M concentration, and dispensed through a 0.1 μm filter onto the substrate and spun at 3000 rpm for 30 s. The samples were then pyrolyzed on a hot plate at 400 °C for 1 min and subsequently crystallized in a rapid thermal annealer at 700 °C for 1 min. The first layer, processed with the above parameters, was highly (100) textured and acted as a seed layer for orientation of the subsequent layers.[7] Following the seed layer thus-created, the deposited films were thermally annealed after every four pyrolized layers. The process was repeated until the required film thickness was achieved (~800 to 950 nm). All films showed pure perovskite phase and strong (100) preferential crystallographic orientation, with the Lotgering factor[10] above 90%.

70 nm-thick, circular Pt top electrodes (diameters ranging from 100 μm to 1 mm) were sputter-deposited and patterned by lift-off. Dielectric and piezoelectric response of the samples were characterized and compared before and after radiation exposure. Low-field dielectric measurements were carried out at 1 kHz and 20 mV_{rms}, using an Agilent 4284 A precision LCR meter. A P-PM2 Radiant ferroelectric test system was used for polarization-electric field (P-E) hysteresis measurements at 1 kHz. The converse, effective longitudinal piezoelectric response ($d_{33,f}$) was measured using an aixDBLI double-beam laser interferometer. Piezoelectric measurements were performed with $V_{ac} = 0.2V_c$ (coercive voltage) at 100 or 1000 Hz under dc electric fields of up to $3E_c$ (coercive field). All measurements were performed on at least 5 electrodes at each radiation dose for statistical relevance.

Two sources were used for Total Ionizing Dose (TID) irradiations: 10 keV X-rays and 3 MeV protons. X-ray irradiation was performed with a Seifert RP149 X-ray probe station, at the Laboratori Nazionali di Legnaro (LNL, Padova,

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Italy). A dose rate of 500 rad(Si)/s was used for X-ray exposure (the doses throughout the work are reported in silicon for comparison with published results on common components). 3 MeV proton irradiations were performed with a Van de Graaff accelerator, also at LNL. A flux of $\sim 3.7 \times 10^9$ p/s cm^2 was used for proton exposure, corresponding to a dose rate of about 5.3×10^3 rad(Si)/s. The high dose rate used for these experiments is not expected to significantly affect the results, since all measurements were performed 10 days after irradiation.

Dose steps of 300 krad, 500 krad, 1 Mrad, and 2 Mrad were used for both X rays and protons. Each quarter of each PZT sample was exposed to a different dose of X rays or protons, while one quarter was used as a (non-irradiated) reference and protected from exposure by thick aluminum shields, to measure intrinsic parameter shifts. During irradiation, the samples were left unbiased and all exposures were performed at room temperature.

The parameters of interest to study the dielectric and piezoelectric response of PZT thin films as measured before and after irradiation are reported in Tables I and II in supplementary[18] information. The low-field relative permittivity (ε_r) of the virgin electrodes before irradiation was approximately 1030 ± 30, with dissipation factor ($\tan\delta$) of $\sim 1.2\% \pm 0.2\%$. Dissipation factors for all samples showed a reduction of less than 0.3% after exposure, independent of the radiation dose. Low-field dielectric permittivity decreased with increased irradiation as shown in Fig. 1(a). A slight reduction in ε_r was also observed in the non-irradiated, control capacitors, which could be resulting from small exposure to radiation due to imperfect coverage of the reference area. A similar trend, i.e., degradation by exposure to radiation, was observed in the overall levels of remanent polarization and effective piezoelectric response of the irradiated samples as shown in Figs. 1(b) and 1(c).

A smaller overall reduction in all of the parameters was observed in the protons-exposed samples compared to the X-ray irradiated ones (see supplementary information, Tables I and II).[18] This might be due to the different underlying events at exposure to different radiation sources. Protons deposit energy in the target material both via ionization processes and via displacement damage. The first mechanism results in the generation of electron-hole (e-h) pairs that might get trapped into pre-existing defects or trigger electrochemical reactions, eventually leading to new defects.[11] The second one generates vacancies and interstitials (point defects or clusters thereof).[11] On the other hand, X rays only deposit energy via ionization processes. The fact that degradation is observed with both sources could suggest that ionization is the primary degradation mechanism in the irradiated samples.

As noted before, radiation doses have been reported in silicon. Since there is no guarantee that doses calibrated in Si are equivalent in PZT, part of the difference between the degradation observed with protons and X rays could be due to the actual amount of energy deposition in the PZT, which may be different for the two radiation sources. Another factor that can explain the larger effects observed with X rays is dose enhancement effects.[11] X rays interact with matter generating electrons via the photoelectric effect, which largely increases with the atomic number of the target material.

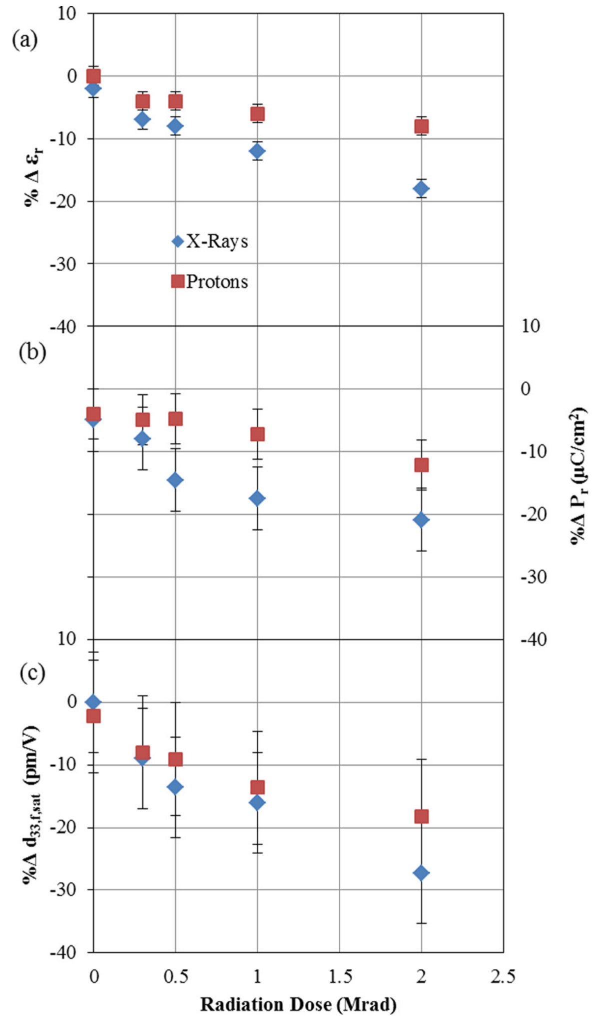

FIG. 1. Percentage change in the (a) low field dielectric permittivity, measured at 0.25 kV/cm and 1 kHz, (b) remanent polarization, measured at 1 kHz, and (c) effective saturated piezoelectric response ($d_{33,f,sat}$) of the PZT thin films, measured at 10 kV/cm AC and 40 kV/cm DC fields and 1 kHz, as a function of radiation dose.

Hence, X rays tend to deposit more energy in heavier materials with respect to lighter ones. In particular, when there is an interface between heavy and light materials, many more electrons will be generated in the heavy material, and some of them will cross the interface due to their random momentum, enhancing the amount of energy deposition in the light material. As a consequence, the Pt electrode may enhance charge deposition at the interface with the PZT during X-ray irradiation. On the other hand, dose enhancement does not occur with protons, and this can explain why larger parametric shifts in the samples irradiated with X rays are observed compared to those irradiated with protons, for the same nominal (Si) dose.

Pinching features were observed in the irradiated samples' minor hysteresis loops (Figure S1 in the supplementary information).[18] Previous observations of such characteristics of hysteresis curves in PZT films have also been attributed to a large concentration of defect dipoles (usually acceptor-oxygen vacancy complexes) in the films.[4] Capacitance-Voltage (C-V) measurements conducted before and after radiation exposure are shown in Fig. 2. Presence of additional peaks, here observed after irradiation, have been associated

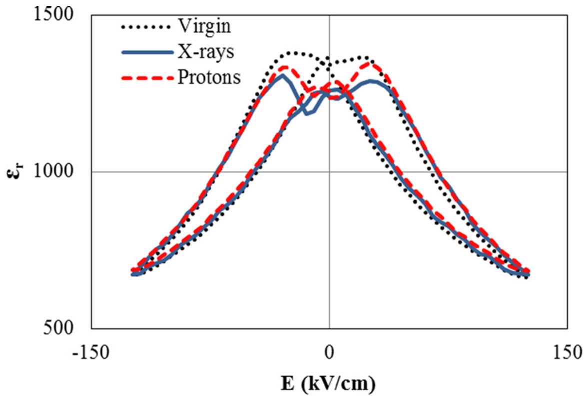

FIG. 2. ε_r-E_{DC} curves for a 810 nm-thick PZT film, in virgin state and after irradiation by 2Mrad X rays and protons (measurements performed at 1 kHz).

in the literature with the presence of more than one polarization switching mechanism, or presence of substantially different switching activation energies (possibly due to different families of pinning sites). Despite lower dielectric response at low bias fields, at high bias fields the irradiated samples exhibited capacitance values very similar to the virgin samples. While extrinsic contributions are a major component of the dielectric response at low bias fields, these are minimized at high bias fields due to the limited domain wall mobility in high poling fields.[12] Therefore, the changes in the C-V curves suggest variations in the extrinsic contributions as a major source of the observed radiation-induced degradations.

In order to further investigate the possible extrinsic origin of the observed degradation in the dielectric response of the radiation exposed samples, nonlinear dielectric measurements were conducted, and analyzed in the framework of the Rayleigh law.[13] The dielectric Rayleigh parameters were $\alpha = 23 \pm 2$ cm/kV (irreversible dielectric Rayleigh parameter) and $\varepsilon_{init} = 950 \pm 50$ (reversible dielectric Rayleigh parameter) at 1 kHz for the virgin samples. The films showed a significant reduction in the irreversible Rayleigh parameter for irradiated samples, escalating with increasing radiation dose (Fig. 3). Intriguingly, while α showed a decrease of up to $\sim$50% at 2 Mrad X-ray exposure, the reversible Rayleigh parameter showed a much smaller reduction of only $\sim$15%. This results in more than 40% decrease in the irreversible to reversible Rayleigh parameters' ratio ($\alpha/\varepsilon_{init}$) after irradiation. $\alpha/\varepsilon_{init}$ can be considered as a quantitative measure of the ratio of the extrinsic to intrinsic contributions to the dielectric response (neglecting the contributions from reversible extrinsic contributions contained in the ε_{init} term). Extrinsic contributions in ferroelectric materials are mostly due to the motion of internal interfaces, such as domain walls and eventual phase boundaries.[13] Pinning and bowing of a moving domain wall in interaction with defects in an electric field have been previously observed by optical, near-field, and electron microscopy.[14,15] Strong pinning of domain walls leads to high activation energy for the mobility of the wall itself. In such case, an applied (ac) electric field will often result in the vibration rather than motion of the domain wall, which therefore contributes only to the reversible Rayleigh parameters. Conversely, weakly pinned domain walls can be "unpinned" by application of high enough external (electric or elastic) fields. Such motion of domain walls is considered to be an irreversible contribution, as requires motion from a local potential minimum to another local minimum, and is reflected in the irreversible Rayleigh parameter.

The expected radiation-induced point defects can also act as additional pinning centers with respect to the domain walls, similarly limiting their mobility under applied electric field and leading to decreased extrinsic contributions. Although the presence of double peaks in the C-V curves (Fig. 2) seems to suggest a substantially different pinning energy associated with the radiation-induced defects, such a behavior was not clearly visible in the nonlinear dielectric curves. This might be possibly due to the low value of the switching fields associated with the radiation-induced defects, which are close to the threshold values for the nonlinear behavior. Additionally, while both ferroelectric and ferroelastic domain wall motion can contribute to the electromechanical response of ferroelectric thin films,[16] the contributions of the ferroelastic domain walls are usually limited in films of thickness close to 1 μm and below.[16] Therefore, it is not unexpected that presence of additional point defects should have larger impact on the piezoelectric response of the samples with respect to the dielectric one.

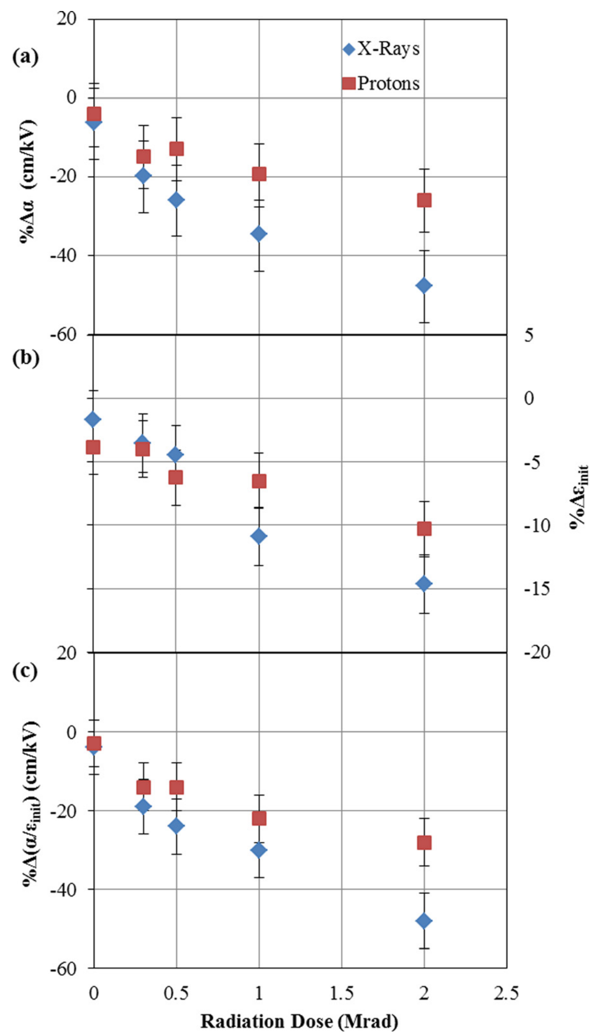

FIG. 3. Percentage changes in the (a) irreversible dielectric Rayleigh parameter, α, (b) reversible Rayleigh parameter, ε_{init}, and (c) the ratio of the irreversible to reversible dielectric Rayleigh parameters, $\alpha/\varepsilon_{init}$ of the PZT films measured at 1 kHz, after exposure to X rays and protons.

To confirm the defect-related changes in the properties of the PZT films, a post-radiation heat treatment at above Curie temperature (450 °C for 10 min in air) was used. The post-heat-treatment samples showed an almost full recovery (within ±3%) of the response. This suggests that the radiation induced defects are recoverable with a heat treatment below the crystallization temperature of the films. Such behavior is consistent therefore with radiation-induced point defects, rather than larger volume-related structural changes, as for example reported for neutron-irradiate PZT films.[17]

To summarize, the effects of X-ray and proton irradiation on the dielectric and piezoelectric response of sol-gel derived PZT thin films as a function of the radiation dose has been studied. Ferroelectric, dielectric, and piezoelectric response of the samples degraded with increased radiation dose and the effect was stronger for the samples exposed to X rays than to protons. Observation of multiple-peaks in C-V curves suggests different polarization switching activation energies, attributed to the presence of radiation-induced defects. Such radiation-induced point defects can act as pinning centers with respect to the domain walls, leading to decreased extrinsic contributions and in turn degraded responses. Nonlinear dielectric measurements confirmed substantial decrease in the extrinsic contributions of the irradiated samples. Results of this study suggest a monotonic decay in the films dielectric and piezoelectric response with respect to the radiation dose, which is recoverable within 3% of the original properties via a post-radiation heat treatment at above Curie temperature. This information can be utilized to predict the operating life-time or to prepare maintenance schedules for devices with integrated ferroelectric films.

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[18]See supplementary material at http://dx.doi.org/10.1063/1.4805045 for the complete set of dielectric and piezoelectric characterization data, before and after irradiation, as well as a sample of the minor hysteresis curves for sample after irradiation.