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Analysis of the degradation induced by focused ion Ga³⁺ beam for the realization of piezoelectric nanostructures

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Piezoelectric nanostructures (islands of dimensions in the lateral size range 50–500 nm) have been fabricated by focused Ga³⁺ ion beam (FIB) etching on PbZr_{0.54}Ti_{0.46}O₃ thin films obtained by magnetron sputtering. The degradation induced by the etching process is investigated through the evolution of electromechanical activity measured by means of local piezoelectric hysteresis loops produced by piezoresponse force microscopy. The analysis of surface potential is performed by kelvin force microscopy and the measurement of current-voltage curves is carried out by conducting atomic force microscopy. Two kinds of structures, namely one based on crystallized films and the other based on amorphous ones, were studied. In this latter case, the amorphous films are postannealed after etching to obtain crystallized structure. For the structures based on the crystallized and then etched films, no piezoelectric signal was registered that evidences a serious degradation of material induced by Ga³⁺ ion implantation. For the structures based on the films etched in amorphous state and then crystallized, the piezoresponse signal was near to that of the reference films (crystallized and not etched) whatever were the ion dose and the island dimensions. Even for very small lateral size (50 nm), no size effect was observed. The island shapes fabricated by Ga³⁺ FIB etching process (islands with less than 50 nm lateral size) show a limitation of FIB processing and electron beam lithography seems to be necessary. © 2010 American Institute of Physics. [doi:10.1063/1.3474963]

I. INTRODUCTION

Piezoelectric nanostructures are currently of the potential interest for the development of microelectromechanical/nanoelectromechanical systems (NEMS). Their main applications in the biomedical domains (microbiosensors/nanobiosensors) and in automobile industry^{1–4} (actuators) are based on PbZr_{0.54}Ti_{0.46}O₃ (PZT) recognized as leading material for these piezoelectric microdevices/nanodevices. The fabrication of piezoelectric nanostructures on pure PZT (or “doped-PZT”) films is frequently performed by means of reactive ion etching (with fluorine and/or chlorine gases), reactive ion beam etching (RIBE), focused ion beam (FIB) Ga³⁺ etching, and electron beam direct writing.^{5–8} To address the quality of the nanostructures, the measurement of local electromechanical activity via piezoelectric hysteresis loops acquisition using piezoresponse force microscopy (PFM) is certainly one of the best options.^{9–16} Typically, the obtained results show that it is possible to fabricate nanostructures with very small lateral size (10 nm on PZT films) but for crystallized films no ferroelectric properties are observed after etching and the piezoresponse is strongly degraded.¹⁷ A postannealing treatment in oxygen results in a partial recovery of the ferroelectric properties.^{17,18} The damaged layer

that appears on the films' surface was thoroughly characterized in terms of the composition and charge implantation but a more detailed characterization seems to be necessary. The main goal of the present study is to evaluate the damage induced by FIB etching of PZT films: implantation of Ga³⁺ and film amorphisation. We focus this work to the development of a suitable process of nanostructures manufacture without introducing piezoelectric property degradation. Here, we present a more effective alternative method to solve this problem.

II. DESCRIPTION OF THE STRUCTURES AND EXPERIMENTAL SET UP

In this work, we have studied two types of Si/SiO₂/TiO_x/Pt/PZT/Pt structures, namely PZT films being either in amorphous or crystallized state before etching. The films in both states are deposited by radio frequency magnetron sputtering without substrate heating and therefore the films were amorphous.¹⁹ The film composition is fixed at the morphotropic phase boundary (Zr/Ti=54/46). A postannealing was used to crystallize the PZT film in the Perovskite phase; the annealing temperature was 625 °C (conventional annealing) in air during 1/2 h.²⁰ The film thickness varied between 100 and 300 nm depending on the island diameter, i.e., for a small island diameter the film was thinner to reduce

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the etching time. A focused beam of Ga^{3+} ions (STRATA DB 235—FEI) was used to pattern the PZT films. The system was equipped with both the electron and ion beams. The advantage of this system is the possibility to monitor the etching process in real time. The acceleration voltage was 30 kV and ion current was in the range 100–10 pA depending on the island diameter. We have studied the relation between the current density of the ion beam and its diameter. The ion beam was at the 90° angle to the etched surface. Before the fabrication of Pt/PZT/Pt islands, we have evaluated the degradation of the PZT material deposited on the entire substrate, using several atomic force microscopy (AFM) techniques, namely, PFM (and its spectroscopic tool which enables the measurement of local piezoelectric hysteresis loops) and kelvin force microscopy (KFM). For such investigations, a commercial AFM (Multimode, Nanoscope IIIA, Veeco) operating under environmental conditions was used. The local piezoelectric hysteresis loops were obtained by plotting the amplitude of piezoelectric vibration A as a function of the dc voltage in so-called “in-field” mode in order to provide information about electromechanical activity. The frequency and the amplitude of the driving ac voltage were $f=2$ kHz and $V_{ac}=1.5$ V, respectively. The applied dc voltage was gradually swept between -10 and $+10$ V within the period of 200 s. To minimize the electrostatic force effect, Pt/Ir coated Si tips/cantilevers with relatively high spring constant of about 45 N m^{-1} were used.¹⁶ PFM domain imaging was also performed using the same cantilevers with the spring constant of 3.8 N m^{-1} (the frequency and the amplitude of the driving ac voltage were $f=8$ kHz and $V_{ac}=1.5$ V, respectively). KFM is a noncontact AFM-based technique based on the electrostatic interaction between the tip and the surface. Surface potential maps are easily detected due to work function variation as a result of surface charges, electric dipoles, or absorption layer. Some authors have shown that PZT before etching becomes GZT (G stands for Ga) after etching.¹⁷ This happens because Pb is preferentially etched (high sputtering yield) and Ga is implanted. Then KFM was used here to analyze the surface of the PZT film. Like PFM, conducting atomic force microscopy (CAFM) is a contact mode technique where a metallic cantilever is connected to a current amplifier. This technique allowed us to measure local electrical conductivity of the material.

III. RESULTS AND DISCUSSION

Actual size of the structure shown in Fig. 1 is $7 \times 7 \mu\text{m}^2$. In order to evaluate the influence of the ion dose, the number of ion beam paths was varied between 1 and 20. According to Ref. 21, the relation between the number of paths and the Ga^{3+} ion dose is the following: the ion dose $=4^{13}$ for one path and it becomes 3^{15} for 20 paths. We have compared the piezoelectric response of three samples: unetched crystallized PZT film [denoted as sample (a)], amorphous PZT film etched before crystallization [sample (b)], and PZT film etched after crystallization [sample (c)]. In crystallized PZT films [sample (c)] we observed strong piezoresponse degradation whatever is the ion dose during

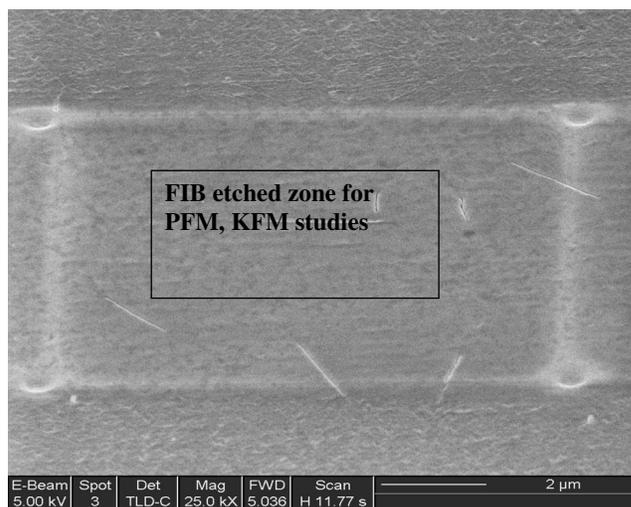


FIG. 1. Scanning electron microscopy (SEM) image of an etched zone by FIB. The dimension of the zone is $7 \times 7 \mu\text{m}^2$. PFM and KFM images are made in this zone.

etching. In fact, no piezoelectric response was obtained even after first path. At the same time no ferroelectric domains could be imaged. We tried to rejuvenate at least partially, the piezoelectric activity using a postannealing treatment [as it is currently proposed in the literature, e.g., for PZT films etched by RIBE (Ref. 22)], but irrespective of the conditions (temperature, atmosphere) we were unable to restore the initial properties of the films. For the sample (b) no degradation was observed and we applied the amorphous process to fabricate very small islands of 50 nm size. The piezoresponse measured for these islands is similar to that obtained for large islands (>500 nm) (Ref. 7) that proves an excellent performance of the process applied. The KFM image of Fig. 2 shows the evolution of the tip grounded CPD (contact potential difference) response as a function of the number of paths on the sample (c). The KFM and the CAFM (see later) measurements were made at the same time that means with CAFM configuration the tip is virtually connected to the ground and the bias is applied to the sample. The change of contrast is, of course, directly related to the variation in the surface properties such as the composition and/or amorphisation of the material and induced structural defects. We cannot make more definitive conclusion for the moment but it is clear that after 20 paths the etched region is completely modified. A CPD profile (here the sample is grounded) over the three etched area indicates almost no modification of CPD for one path and apparent decrease by 350 mV and 500 mV for 10 and 20 paths, respectively. In our conditions (room and instrument calibration), the CPD of the surface was -50 mV relative to a sample grounded. To compare the KFM signals obtained on the samples (b) and (c), we perform a second experiment under the same condition (tip, instrumentation configuration, and sample grounding). The results are presented in Fig. 3(a). The strong contrast difference in the sample (c) (between etched and not-etched areas) confirms the strong damage induced and a consequent modification of the surface potential. On the contrary, only weak damage (small contrast variation) is observed for the sample

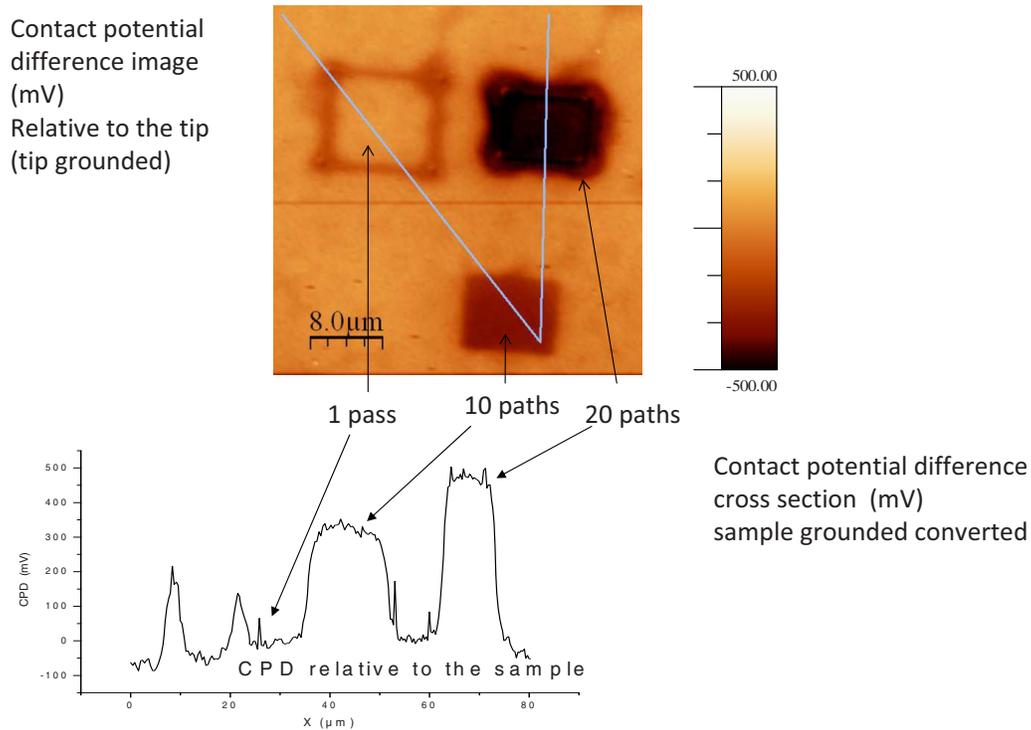


FIG. 2. (Color online) KFM signal on sample (c) measure on areas subjected to different number of paths.

(b) (etched in the amorphous state). To point out these variations more clearly, we indicate the CPD value across the etched region [Fig. 3(b)]. It confirms that the potential increase between the unetched surface and the surface of PZT

etched after crystallization is very large (about 300 mV). The implanted charges are the same in both samples but for amorphous sample we can suppose that the annealing treatment induces these charges neutralization and a slight de-

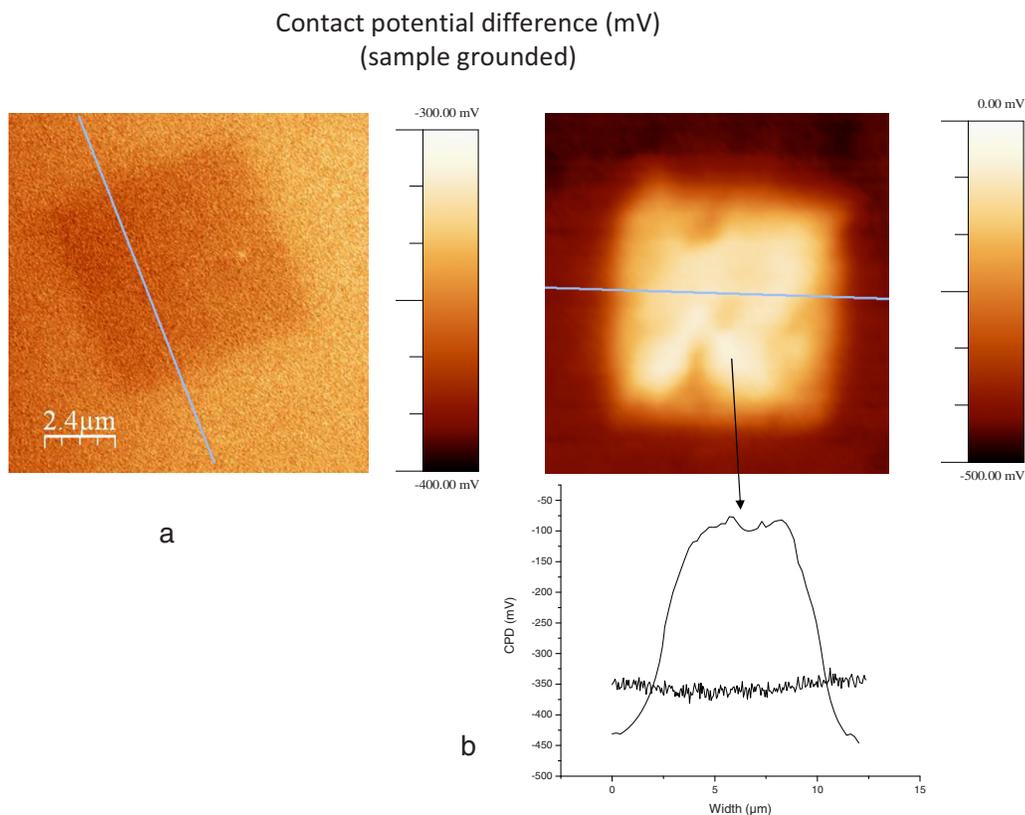


FIG. 3. (Color online) (a) KFM signal measured on amorphous and crystallized film after etching. (b) Cross-section of the contact potential measured sample (c). The position of the scan is shown in (b).

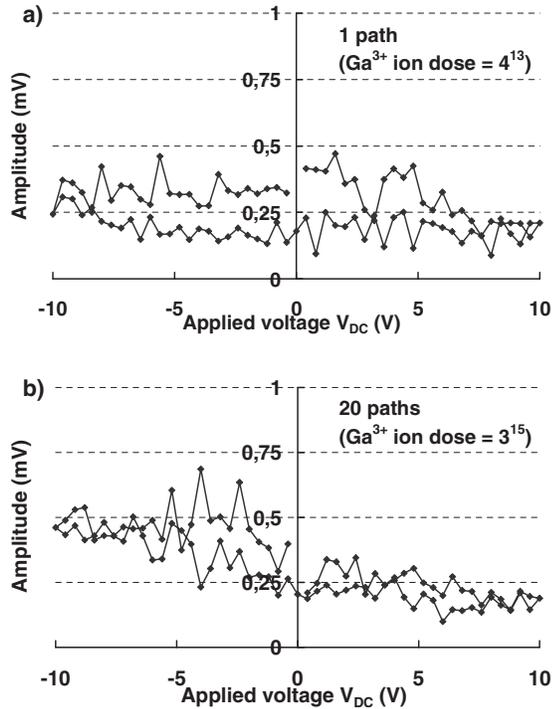


FIG. 4. PFM hysteresis (amplitude vs dc bias) of etched zone of sample (c) (crystallized PZT) after one (a) and 20 paths (b).

crease (10 mV) of the CPD is only detected. The properties of the etched area are certainly different depending of the process. The difference, in terms of material is not only due the presence of charge on the sample surface but some crystal defects (dislocations), substitution between Pb and Ga,¹⁷ implantation of metallic Ga³⁺ probably were maintained on sample (c) but not in sample (b) due to the annealing treatment. Figure 4 shows the piezoresponse amplitude A measured on etched zone after one path and 20 paths in the sample (c) (etched after crystallization). As we can observe, only weak piezoelectric activity is obtained even after one path. The poor ferroelectric properties are confirmed by the absence of the hysteresis on both samples. Therefore, the FIB etching is detrimental to functional properties of PZT. Annealing of these etched zones (in air or in O₂ atmosphere at different temperatures and times) had no effect on piezoresponse. On the contrary, for PZT etched before crystallization [sample (b)], the piezoelectric signal (measured after crystallization) is the same as the one obtained for the sample (a) irrespective of the ion dose. Even if degradation is induced on the sample (b), the annealing treatment (crystallization of the film) permits to eliminate the damages. These results confirm that the strong degradation occurs on the initially crystallized samples and no degradation happens if the FIB is conducted on amorphous samples. So, we have applied the FIB process developed for the sample (b) to fabricate PZT nanoislands. The typical structures obtained by SEM are shown in Fig. 5. The size of the island shown in Fig. 5(a) is 50 nm and dimensions of 250 × 250 nm² were realized for a square island [Fig. 5(b)]. A Pt top electrode was used as a mask to protect the top of the island and, therefore, we take into account only the defects introduced into the islands walls. The etching anisotropy [angle α equal

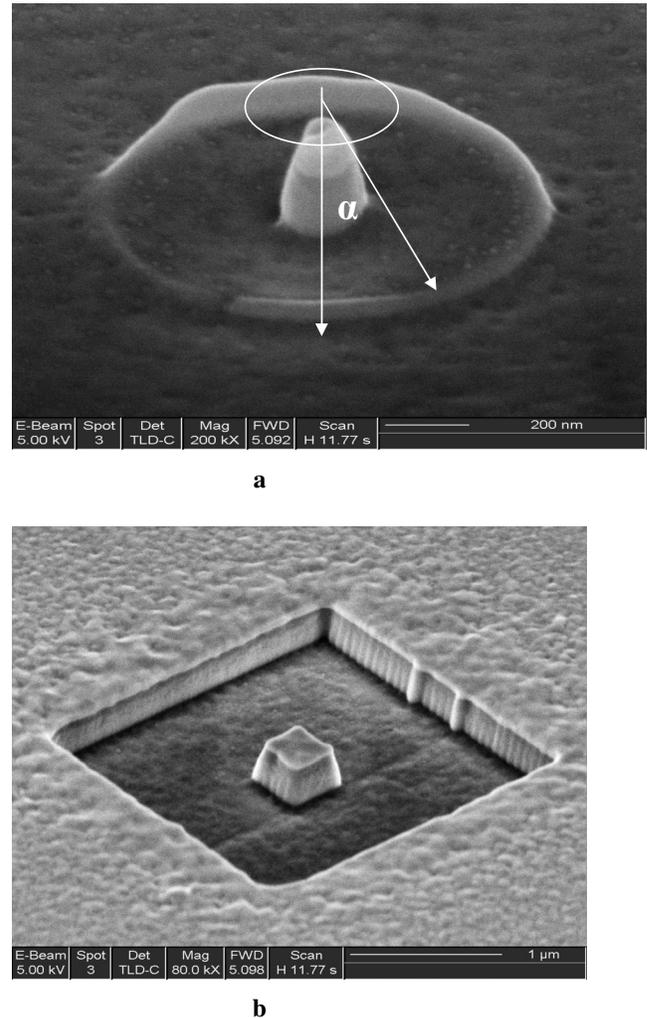


FIG. 5. (a) SEM of a typical PZT island of 50 nm in diameter fabricated on sample (b) (amorphous PZT). The angle α is related to the etching selectivity between Pt and PZT. (b) SEM of a typical square PZT (250 × 250 nm²) fabricated on sample (b).

to 45° in Fig. 5(a)] is observed probably due to the selectivity between Pt and PZT. This etching anisotropy and the wall slope could be a limitation of the FIB process applied. Electron beam nanolithography is currently in progress to fabricate island with the lateral size below 50 nm (always with using a Pt mask). The comparative results of the PFM measurements on the PZT islands of 50 nm of size are shown in Fig. 6. It can be concluded that the piezoresponse amplitude is similar to that obtained for a larger island.⁷ This figure shows that the PFM signal obtained on 50 nm island [sample (c)] has weak piezoelectric activity both before and after recovery treatment in O₂ atmosphere (we also used a Pt mask in this process). The signal could not be restored after post-annealing. These results contradict to those obtained by Stanishevsky *et al.*¹⁷ where the acceleration voltage of Ga³⁺ ions is larger (50 kV) and so it had to induce stronger degradation. In order to explain why the piezoelectric signal disappeared under etching we have performed a local I (V) measurements with CAFM on a similar PZT island [sample (c)] but of 250 nm lateral size. The result is shown in Fig. 7. For these experiments, a dc bias was applied to the substrate holder and the top surface Pt was connected to the current

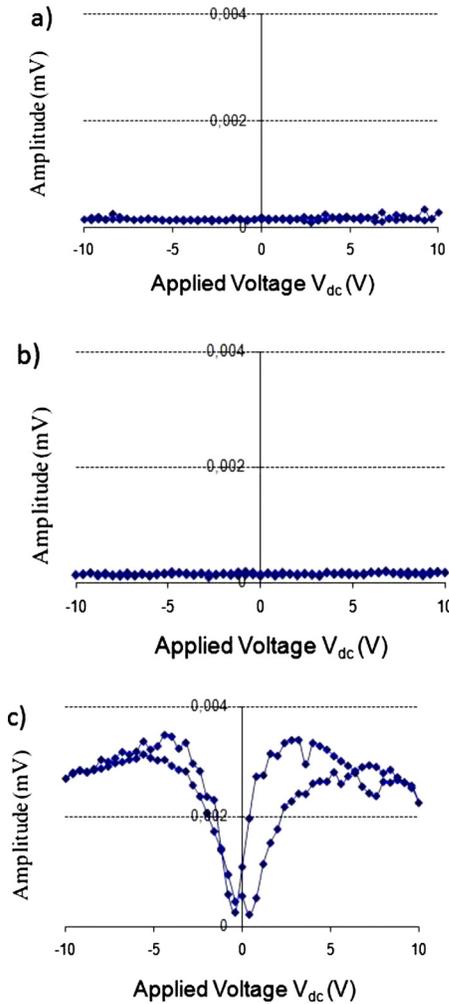


FIG. 6. (Color online) PFM signal (amplitude) measured on PZT islands of 50 nm in diameter after (a) conventional etching process, (b) postannealing at 625 °C under O_2 , and (c) amorphous FIB etching process.

amplifier through the tip. The current increased rapidly with the applied voltage indicating strong local conductivity due to the presence of an electrical conducting channel. This proves a very strong damage due to Ga^{3+} ion implantation in the crystallized PZT nanoislands (in particular on the island wall) and associated loss of the piezoelectric activity.

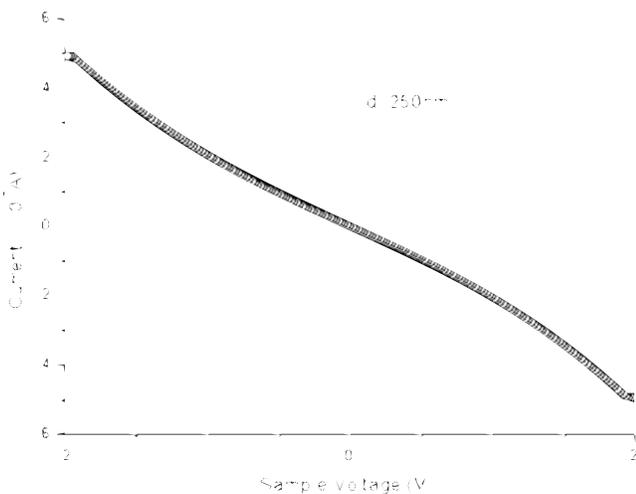


FIG. 7. I (V) measurement on sample (c) obtained by CAFM.

The current density is in the order of maximum density of metallic material without degradation but depend of the joule heating. We believe it does not damage the sample because the characteristics were reproducible. Note that if it is destructive with I (V) then it should be destructive under PFM cycle too (samples are biased in the same manner without protection, in the case of CAFM, the current is limited by the gain of the amplifier to 500 nA). This observed conductivity increase is thus responsible for the weak electromechanical activity observed previously on the etched zone of the sample (c). It can be thus stated that our FIB process performed on amorphous films is very convenient for the fabrication of piezo-NEMS. The apparent size effects in nanoscale ferroelectrics are a challenge^{23–26} and the described process can be a base for further miniaturization.

IV. CONCLUSION

In conclusion, in this work we have evaluated the damages induced by FIB for two different kinds of nanostructured PZT films being in amorphous or crystallized state before etching. In crystallized PZT films the damage is very strong and no piezoelectric response is measured even after a postannealing treatment. In the films where the etching is done in the amorphous state, no degradation is observed. The latter process is used to fabricate PZT islands. In 50 nm size island the piezoresponse is not changed in comparison with unetched PZT films. To decrease the size of the island below 50 nm the FIB process is limited due to the observed etching anisotropy and future nanofabrication of small nanoislands (<50 nm) can be possibly achieved using electron beam lithography.

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