Scientific Report of Vittorio Foglietti
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Defective interfaces in Yttrium-doped Barium Zirconate films, characterization of the transport properties by scanning probe techniques

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Yttrium doped Barium Zirconate (BZY) films have been grown by PLD at home institution (SPIN-CNR). The films have been deposited on a substrate with a large lattice mismatch (NGO) and a second substrate with a good lattice matching (MGO). Various samples of thicknesses for each substrate have been deposited. One thickness is above the critical value for strain relaxation: 100nm and the second thickness is 15-20 nm, which is the thickness, which shows the most interesting transport properties. The film mosaic spread has been examined by the rocking curve technique, the surface morphology checked by scanning electron microscopy and the strain state investigated by XRD. We have conducted and experimental investigations mainly by Electrochemical Strain Microscopy (ESM), which has been used to detect electrochemical activity in BZY films with nanoscale resolution. This technique leads us to the question we plan to address: *to find a clear correlation of high values of carrier diffusion coefficient with the presence of a defective interface and derive an analytical expression, which relates the ESM relaxation times with carrier diffusivity.* With pulsed bias, electrochemical reactions and ionic migration is activated using a set of rectangular bias pulses of defined voltage amplitude. Specifically, after each voltage pulse, the tip potential is returned to zero. The waveform consists of a train of 100 ms long bias pulses with an amplitude-modulated voltage peak. The envelope of the amplitude modulation is a slowly varying (0.05 Hz) triangular waveform.

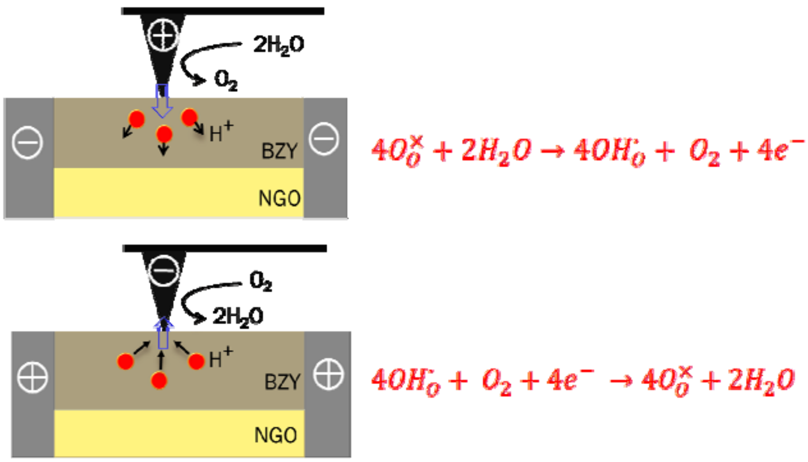

Figure 1. Electrochemical reaction activated during a) positive bias and b) negative bias of the tip.

By increasing the amplitude of the bias applied to the tip above a threshold voltage, the electrochemical reactions of figure 1 are activated leading to ion defects injection. When the pulse voltage is slowly decreased down to zero, the film will experience a remanent ion excess, similarly to the residual magnetization in ferromagnetic materials. If the envelope of the pulse is a triangle with voltage mean value equal to zero, the overall balance of the ions injected in the film is expected to be zero. We performed a systematic tracing of the evolution of loops by progressively increasing the peak bias voltage *Vp* of the triangular waveform cycles. This last technique is called First Order Reversal Curve (FORC), where the term “first order” is used to emphasize the fact that each of these curves are formed after reversing of the input. The FORC measurements enable accurately monitoring the onset of the ion injection by measuring the ESM strain signal evolution while the excitation waveform is applied to the tip. An example of an envelope waveform used in our measurements is shown in Figure 2. In the example figure, there are 5 triangular cycles, with the maximum voltage peak increasing in every cycle. The strain signal is measured after each pulse step. The ion injection or extraction results in a localized strain under the tip, which can be detected through dynamic surface displacement. The ESM is an extremely powerful technique, allowing monitoring the voltage threshold required to inject ions and film topography. Injection of ions happens almost adiabatically,

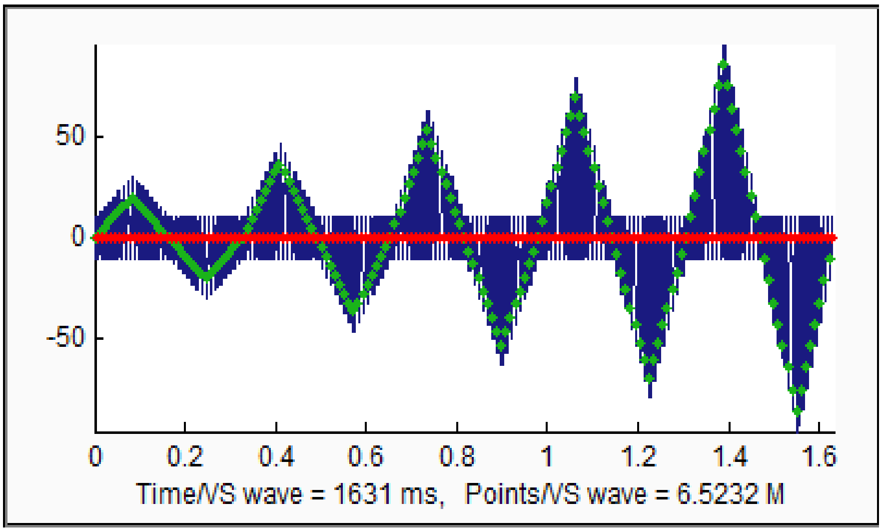

Figure 2. The measurements were performed with films deposited on different substrate using the following FORC waveform

The FORC measurements were performed vs temperature and in wet and dry conditions. A result example of the performed measurements is shown in figure 3. From these FORC measurements we can extract the finger print of the transport mechanism: the activation energy. So we can identify different transport mechanism acting on our thin films. A very important parameter in protonic conductors is the diffusivity. If the diffusion coefficient is known then the mobility of the carriers can be deduced from the Einstein-Smoluchowsky relation. There are various possible mechanisms for proton diffusion in our Barium Zirconate thin films, depending on the film thickness and different related physical process. The kinetics of the Electrochemical Strain Microscopy is controlled by the diffusion times of the carriers, and is therefore expected to be relaxational in nature. With a proper choice of the experimental set-up, we can relate the ESM signal relaxation to the carrier diffusion coefficient. Relaxation measurements enable determination of diffusion coefficient which is related to the mobility of the transport process.

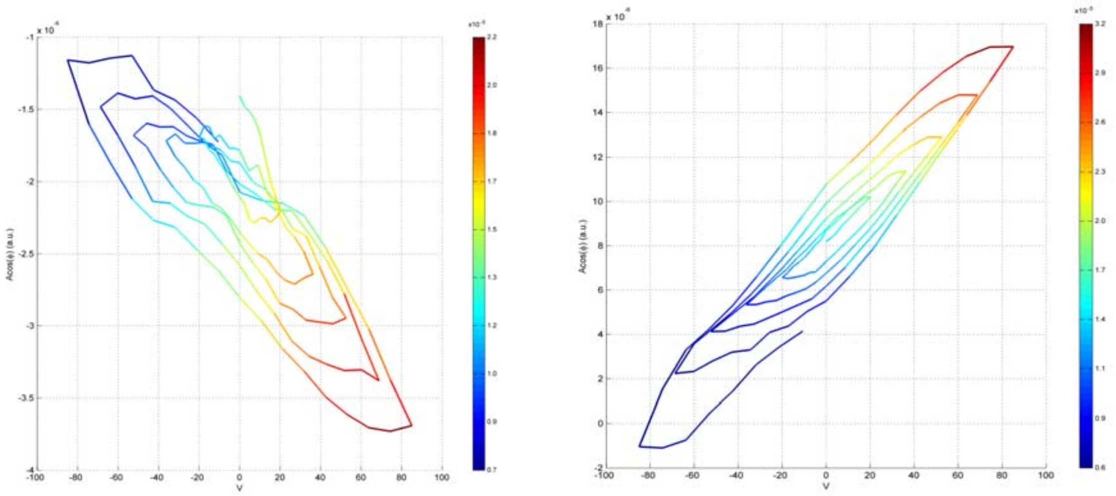

Figure 3. Example of FORC measurements on different BZY films.

We performed strain relaxation measurements vs temperature and in wet and dry conditions. Assuming that a) in presence of different charges (ambipolar diffusion), the measurement is related to the slowest (low mobility) charge carrier; and b) in case of single charge the mechanism is a combination of drift and diffusion, the analysis of the ESM amplitude vs time will enable us to determine with good accuracy the value of the diffusion coefficients. For example, a two dimensional diffusion mechanism, which is typical of a very thin film, should proceed as t-1 while a three dimensional diffusion process is usually described by t-3/2 behavior. We have recorded a sufficient amount of data to find a quantitative correlation between the diffusion coefficient and the ESM relaxation signal. An example of the relaxation measurements are shown in figure 4. We just started the data analysis that will enable us to publish the significant results of this work.

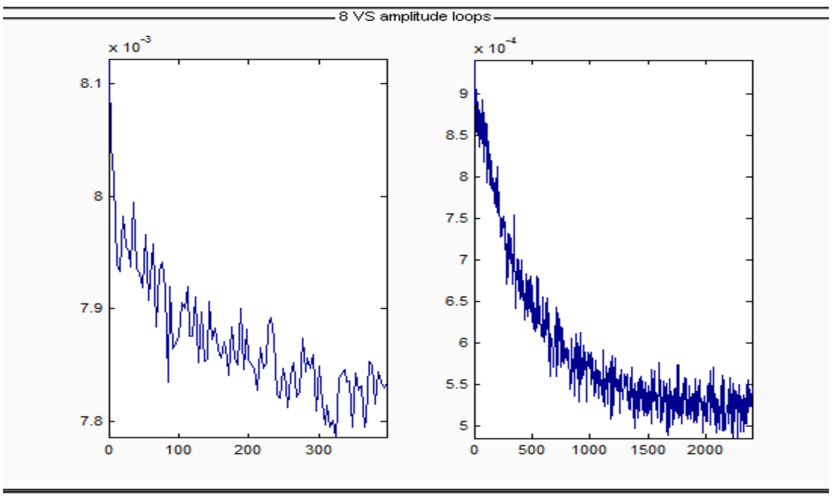

Figure 4. Example of relaxation measurements s on different BZY films.