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A R T I C U L O

Modification of a commercial nanoindentation system for measurement of hysteresis cycles under mechanical load in polycrystalline ferroelectric films

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A commercial hardness-tester by nanoindentation was modified to use metallic indenter tips for the measurement of hysteresis cycles of ferroelectric films under mechanical load and with high lateral resolution. A novel semi-automatic charge integrating module was developed to this aim. LabVIEW 8.6 graphical programming environment was used to control the data acquisition system (DAS), the sinusoidal high voltage generator (± 300V) and the charge integrating module in the measurement of the loops. The software also provides data correction due to non-ferroelectric-switching contributions to obtain reliable remanent polarization (P_r) and coercive field (E_c) values. It also displays the loops both in polarization-field (P-E) and current density-field (J-E) modes. The experimental set-up was validated with measurements on dense PZT films (10μm) on platinised Si substrates. Coherent cycles are obtained using the novel semi-automatic charge integrator , the classical Sawyer and Tower circuit and using an electrometer. Under low indentation load causing quasi-elastic strain, the loops do not show any artifact.

Keywords: Nanoindentation; Polycrystalline Ferroelectrics; Films; Hysteresis loops; Data acquisition systems

Modificación de un nanoindentador comercial para medir los ciclos de histéresis ferroelectrica bajo la accion de una tensión mecanica en capas poliscristalinas

Se ha modificado un nanoindentador comercial para el uso de puntas metálicas para la medida de ciclos de histéresis en láminas ferroeléctricas bajo carga mecánica y con alta resolución lateral. A este fin, se ha desarrollado un circuito integrador de carga semi-automático. Se ha utilizado el entorno de programación gráfica LabVIEW 8.6 para el control del sistema de adquisición de datos (SAD), un generador de alto voltaje sinusoidal (± 300V) y el circuito integrador en la medida del ciclo. El software desarrollado también realiza la corrección de los ciclos por sustracción de las contribuciones no debidas a la inversión de la polarización ferroeléctrica en la obtención de valores fiables de polarización remanente (P_r) y campo coercitivo (E_c). La representación del ciclo puede hacerse como polarización-campo eléctrico (P-E) o como densidad de corriente- campo eléctrico (J-E). El sistema se ha verificado mediante la medida de ciclos de histéresis en láminas densas de PZT (10μm) sobre sustratos de silicio recubierto con platino. Se ha obtenido resultados coherentes en las medidas utilizando el integrador de carga, el clásico circuito de Sawer y Tower y un electrómetro. Se ha comprobado que no hay artefactos en la medida cuando esta se realiza en el nanoindentador bajo pequeñas cargas que generan deformación cuasi-elástica.

Palabras clave: Nanoindentación; Ferroeléctricos policristalinos; Láminas; Ciclos de histéresis; Sistemas de adquisión de datos

1. INTRODUCTION

Nanoindentation technique for determining hardness and elastic-modulus in films was developed in 1992 [1] and it is widely used in the study of mechanical properties with high lateral resolution. At present there are a number of commercial hardness-testers based on such a technique that, properly modified for the use of metallic spherical indenters and application of electric voltage, can be used for the simultaneous mechanical and electric test of ferroelectric materials.

We have made the needed modifications of the nanoindenter head of a commercial hardness-tester, and based on previous experience [2] installed an experimental set-up including a novel semi-automatic charge integrating module, and developed the appropriated software for data acquisition and analysis to measure ferroelectric hysteresis cycles in films under a sinusoidal bipolar voltage signal.

This work will describe the measurement system and present results on hysteresis cycles of thick lead titanate-zirconate (PZT) dense ceramic films, previously to and under the application of a mechanical load. A comparation of results using the classical Sawyer-Tower circuit, the integrated current density-electric field loops measured using and electrometer and the charge integrating module are also provided.

(a)

(b)

(c)

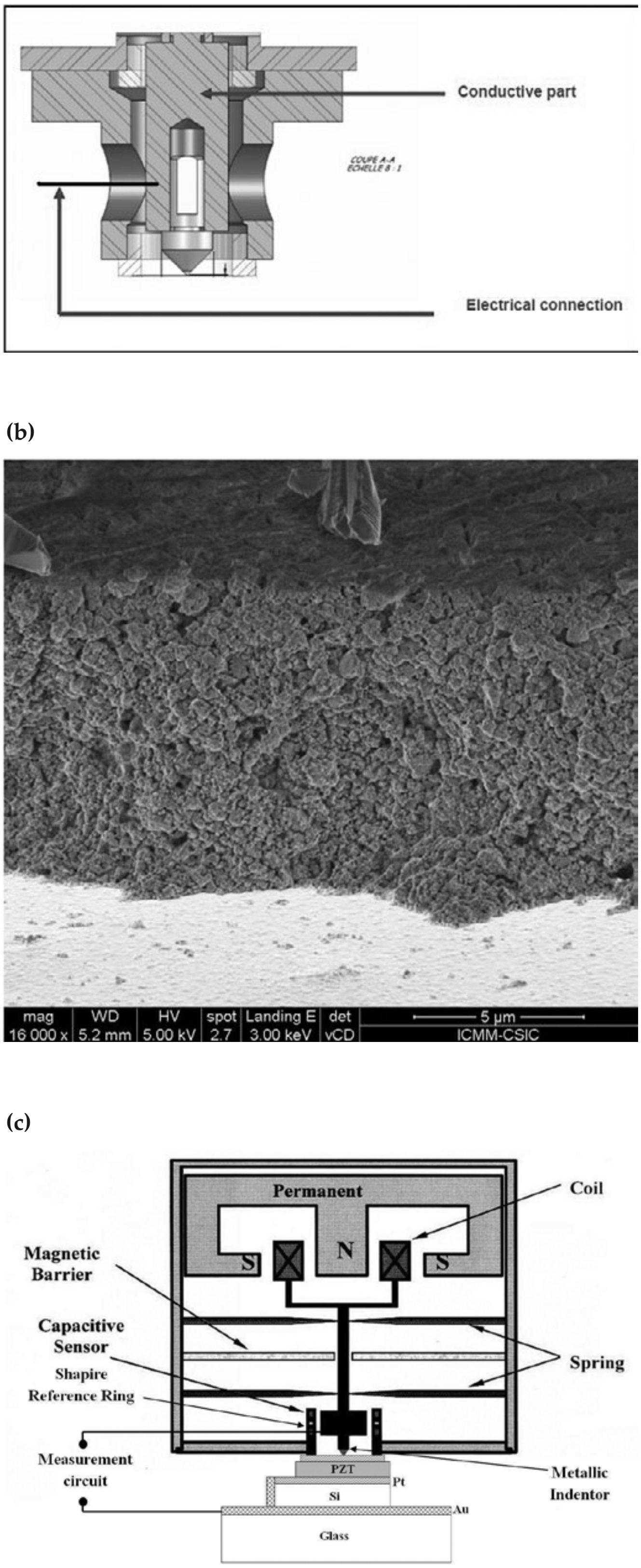

Fig.1. (a) Hardness-tester head modification, (b) aspect of the PZT dense thick film and (c) schematic of the sample connections for the measurement under mechanical load.

2. EXPERIMENTAL

2.1. Modification of a commercial nanoindentation system for the application of electric field to polycrystalline ferroelectric films

Commercial nano-hardness testers by indentation method use hard tips that are usually from electrically isolating materials (diamond). The head of the commercial apparatus [3] was modified so as to be able to use metallic tips with appropriated electrical isolation from the head mechanism and new reference ring for the contact (Fig. 1(a)).

The measurements were carried out on thick films (10μm) of lead titanate-zirconate (PZT) (Fig. 1(b)). Films were obtained by deposit onto platinised <100> silicon wafer of a composite slurry containing PZT powder (PZ26 Ferroperm Piezoceramics, Denmark) mixed with PZT sol to create the bulk of the PZT layer. Due to its high porosity, the slurry is infiltrated with a PZT sol diluted with 2-methoxy-ethanol, with 1:1 ratio, to increase densification to 7.07 g cm^{-3} [4,5]. After drying and pyrolisis, films are treated at 720ºC.

Hysteresis cycles under indentation were measured using a metallic indenter tip as upper contact to the upper electrode of the film. Indentation was made positioning the films on an ordinary glass block with Au sputter-coated flat surface, which acts as lower connector and was short-circuited to the lower electrode of the film (Fig. 1(c)).

2.2. Experimental set-up for the hysteresis cycles measurements

HARDWARE DESCRIPTION

For the hysteresis cycles measurement a PC (Pentium 4, 2.40GHz processor), a Data Acquisition System (DAS) Keithley KPCI-3116 [6] and in-house made bipolar high voltage generator and novel semi-automatic charge integrating module were used (Fig.2). For the sake of comparison measurements were also carried out using and commercial (Keithley 427) [7] current amplifier or electrometer [8,9] and a Sawyer-Tower circuit [10] (Fig. 2).

The in-house made [11] bipolar high voltage generator can be PC controlled via RS232. It generates pulsed or continuous sinusoidal signals of 0,01 to 10 Hz frequency and voltage of ±10V to ± 300V.

The novel semi-automatic charge integrating module was made as a modification of a one previously reported [11] and uses the same integrated circuit (IC CA3130). As a novelty, it was added a digital control interface via a PC parallel port (LPT1) to select the appropriated capacitor (from 10nF to 15μF) for the IC feedback, which makes it a semi-automatic module (Fig. 3).

Due to the very high impedance of the IC, as in a Sawyer-Tower circuit, the current through the sample is the same as the current through the selected capacitor. For a Sawyer-Tower circuit or the electrometer method, the total charge/current measured has, in addition to the ferroelectric-switching component (FE), an ohmic component (due to the resistance R of the film) and a capacitive component (due to the capacitance C of the film) ($i_t = i_{FE} + i_R + i_C$).

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The advantage of this charge integrating module is that it allows measuring ferroelectric hysteresis loops in a non-perturbative way, since the ohmic component of the current is suppressed in the open circuit after the sample [12].

A surge protective circuit based on Zener diodes was added at the entrance of the signal from the sample, to avoid the damage of the charge integrating module and the DAS in the event of the electrical breakdown of the sample under the high field that is needed to apply for the ferroelectric cycle measurement.

SOFTWARE DESCRIPTION

The software was entirely developed within the LabVIEW 8.6 [13] graphical programming environment to control the DAS, the high voltage generator and the charge integrating module in the data acquisition process. In addition, the software has functionalities to store the data in appropriated files, to process the data and to display the measured hysteresis cycles, calculating back and forth from polarization (P-E) cycles to current density (J-E) cycles.

This software is adapted from the software package previously developed [2] to measure hysteresis cycles in thin ferroelectric films. The package is divided in three parts. First, it provides the input with the parameters on the sample geometry (thickness and electroded surface) and the voltage signal (frequency, amplitude, type of signal) and integrating capacitor to be used in the measurement. From these, the needed commands to the DAS, the voltage generator and the charge integrating module are generated. When the voltage needed is below ±10V, the software also contains a control module to be used with an Agilent 33120A [14] signal generator replacing the high voltage

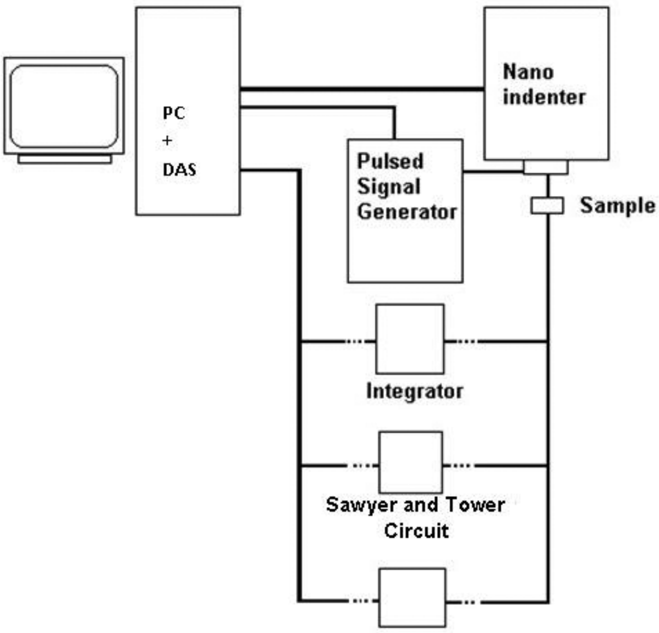

Fig. 2. Block diagram of the circuits for the ferroelectric hysteresis loop measurement.

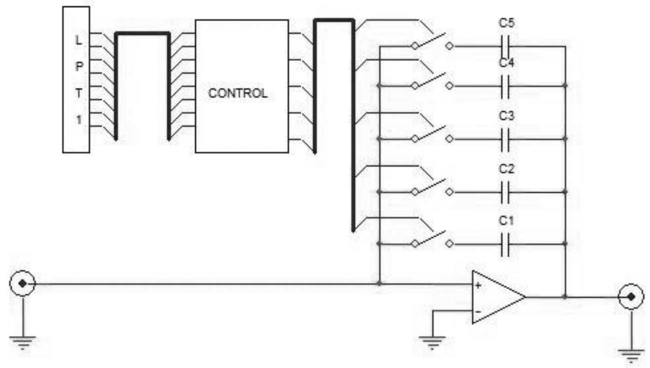

Fig 3. Block diagram of the semi-automatic charge integrating module.

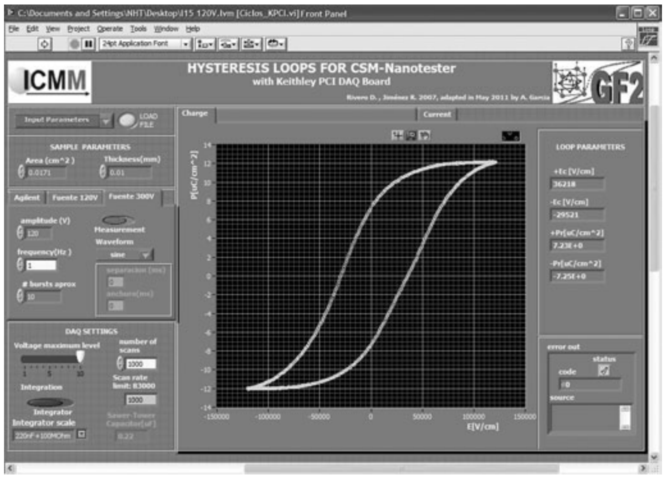

Fig 4. Screen dump of the main panel of the software for the measurement.

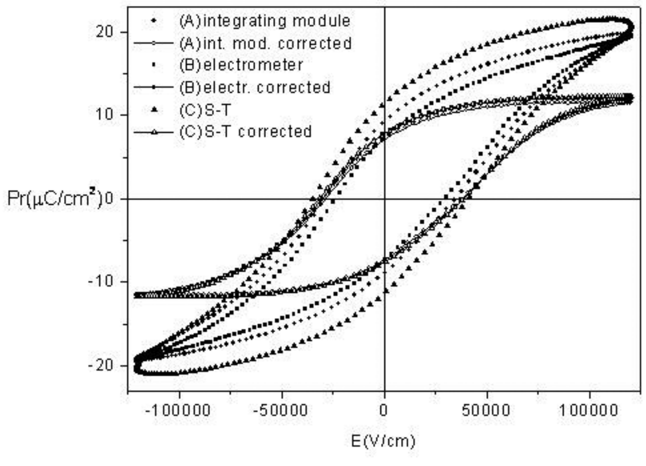

Fig.5. Ferroelectric (P,E) hysteresis loops, as-measured and after corrected from non-switching contributions, measured outside the hardness-tester.

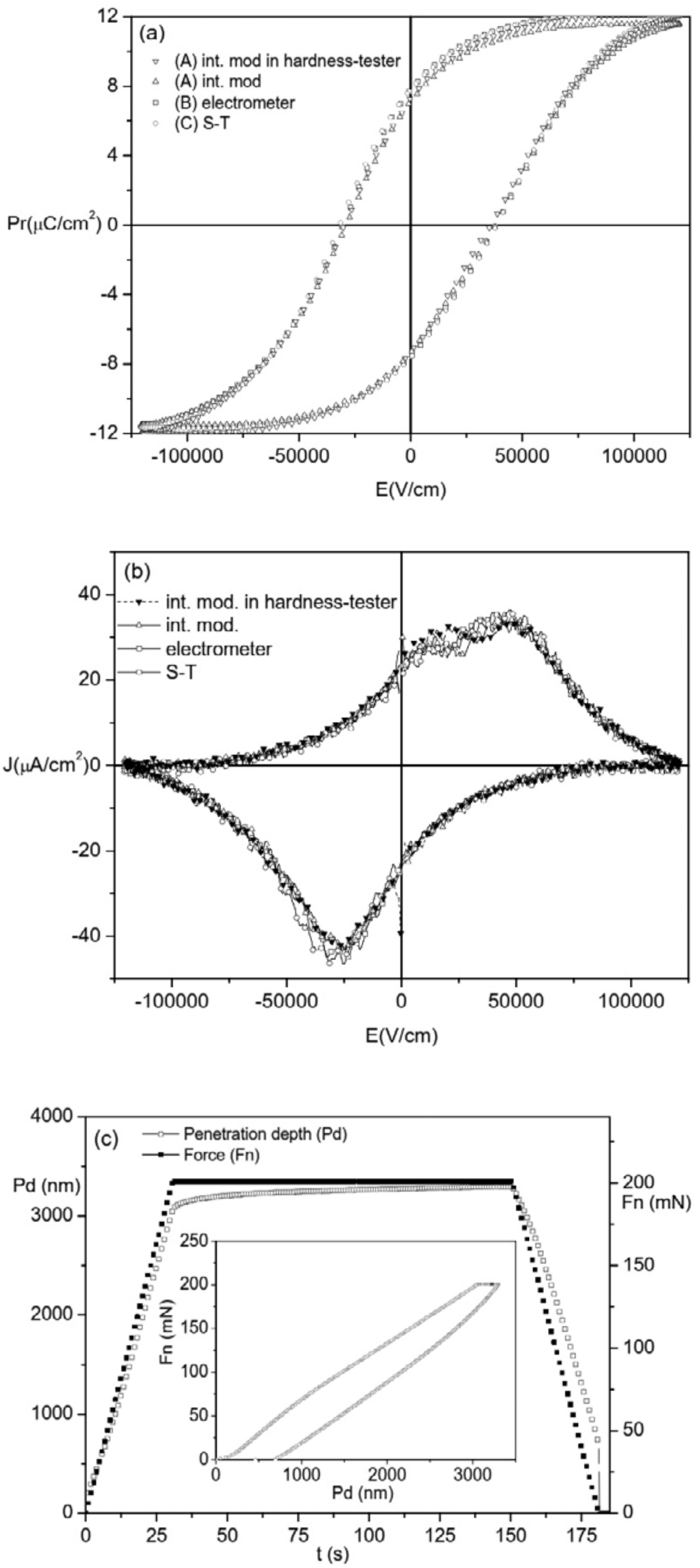

Fig.6. Ferroelectric (a) (P,E) and (b) (J,E) hysteresis loops, as-measured and after corrected from non-switching contributions, measured outside and in the hardness-tester. (c) Load profile used during the measurement in the hardness-tester with the load-penetration curve shown as an inset.

generator. The second part of the program controls the different components of the measuring circuit for the data acquisition. The third part provides data processing and display functions. Fig. 4 shows the screen dump of the main panel of the software package for the measurement.

The main part of the data processing is the correction of the cycle from capacitive and ohmic current contributions in order to obtain a reliable value of the remnant polarization (P_r) and coercive field (E_c) of the film. This is done by a trial and error graphical method [15] considering different values of the R and C of the sample and using the equation:

$$i(V) = i_{FE} + i_R + i_C = S\frac{dP}{dt} + \frac{V}{R} + C\frac{dV}{dt} \qquad (1)$$

3. RESULTS

3.1. Hysteresis cycles of unloaded samples

Fig. 5. shows the hysteresis cycles measured with the semi-automatic charge integrating module (method A), by integration of the current density-voltage loop recorded using an electrometer (method B) and by the classical Sawyer-Tower circuit (method C). All cycles were obtained using a sinusoidal voltage signal of 1Hz. Both directly acquired loops and those corrected from capacitive and ohmic currents are shown.

As expected, directly acquired loops by the method C involve the highest integrated charge. Loops obtained by methods A and B are virtually identical. Loops are slightly asymmetric, which it is expected from films on substrates, due to the stress gradient from the film-substrate interface. The measured loops, previously to the corrections, are in agreement with those reported in the literature [16].

3.2. Hysteresis cycles under mechanical load

Fig. 6 shows the corrected hysteresis cycles, (P,E) and their equivalent (I,E), under mechanical load compared with those measured outside the hardness-tester. We have tested moderate loads applied with a metallic spherical indentor tip of a high radio of curvature to minimize the effect of the load with the aim of testing that the hysteresis measurement using as upper electric contact the indenter tip does not show any artifact. In an indentation experiment, first the indenter tip make the contact with the surface and then the load is increasingly applied, reach the maximum value in 30s, it is maintained during a given time and then removed, again, in 30s. In the experiment the penetration of the tip is recorded as a function of the load at each step (Fig. 6(c)). We maintain the mechanical load during 120 s, which allows measuring 2-3 cycles, as the software for the hysteresis loop measurement is launched independently of the harness-tester software.

Comparison between Figs. 5 and 6 shows clearly that, as expected, for such an indentor and such a load level, the measurements previously to and after the application of the load are virtually identical.

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4. CONCLUSIONS

A commercial hardness-tester by nanoindentation was successfully modified for the measurement of hysteresis cycles under mechanical load with high lateral resolution. A novel semi-automatic charge integrating module and appropriated software using LabVIEW 8.6. for data acquisition, analysis and display of ferroelectric hysteresis cycles were developed.

The experimental set-up was validated with measurements on dense PZT films on platinised Si substrates. Coherent cycles are obtained using the novel semi-automatic charge integrator and the other methods tested, once the proper corrections for non-ferroelectric-switching contributions are carried out. Under low load indentation causing quasi-elastic strain, the loops do not show any artifact and the obtained loops are identical to those obtained outside the hardness-tester.

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El presente libro aparece por la necesidad actual de fomentar y difundir el conocimiento de los Biomateriales, debido a su gran importancia económica y sanitaria, así como por su gran repercusión social.
Su contenido está basado en los cursos internacionales impartidos por la Red CYTED VIII.J, para estudiantes de Ciencia de Materiales, Ingeniería, Biología, Odontología, Medicina, etc., así como para profesionales de dichas disciplinas.
El libro cubre, de una manera condensada y didáctica y con amplia bibliografía, las principales familias de los materiales actualmente empleados como Biomateriales así como aquellas aplicaciones más representativas de los mismos.
El carácter multidisciplinar de los Biomateriales justifica que en su elaboración hayan participado destacados especialistas: (físicos, químicos, biólogos, ingenieros, traumatólogos, odontólogos, patólogos, etc.), lo que contribuye a una visión amplia y actual de la problemática de dichos materiales.

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