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Microstructural and electrical properties of nanocomposite PZT/Pt thin films made by pulsed laser deposition

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Abstract

Dual phase composites made by dispersing a metallic phase into a ferroelectric matrix are of great interest due to significant enhancement in the dielectric constant (ε). In this study thin films of nano sized platinum (Pt) particles were embedded in a crystalline lead-zirconate-titantate (PZT) matrix, using pulsed laser deposition. The microstructure of these films was characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM) and atomic force microscopy (AFM). The electrical properties were investigated by capacitance versus voltage (*C*–*V*) and leakage current versus voltage (*I*–*V*) measurements. The influence of the Pt dispersoids on the crystallinity of the PZT matrix and the dielectric properties of the composites are discussed. Pt addition caused significant changes in the electrical properties, which showed the difference from what is observed for bulk PZT/Pt composites.
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1. Introduction

The dielectric constant of ferroelectric materials can be significantly enhanced by fine dispersion of a metallic phase in the isolating (ferroelectric) matrix. This enhancement is at a maximum just below the percolation threshold, above which the conducting second phase forms a continuous network [1]. Such a composite material could be of importance for a large range of applications in electronic industry, such as high density DRAM (dynamic access memory), non-volatile memory (NRAM), sensors, controlling devices, charge storage devices, antenna systems, etc.

In PZT/Pt bulk composites with 25 vol.% Pt, a factor 4 enhancement in the dielectric constant has been observed [2,3]. After sintering at high temperature (1150 °C) both the PZT and Pt-phases show the crystallographic properties of the pure phases. Of note are the slight decrease in density of the composites and a decrease in grain size of PZT phase with increasing Pt contents. Probably the difference in sinter-ability between PZT and Pt is the cause of the lower density. The location of the Pt particles at the PZT grain junctions also inhibits the grain growth of the PZT matrix. Issues to be addressed are the effect of the microstructure of the composite on the enhancement in the dielectric constant, such as the influence of the ratio between the particle size of conducting and insulating phases. In a previous publication, a novel sol-precipitation route was presented [3], which started with 5 nm sized Pt particles and 300–400 nm PZT particles. After sintering at 1150 °C, however, the particle size of both PZT and Pt increased to a few μm.

Aim of this work is to prepare thin films of PZT/Pt composites with particle sizes for each phase scaled down to the nanometer range. Several techniques are available for the preparation of thin films of PZT, e.g. sol–gel processing, chemical vapor deposition (CVD), (rf-) sputtering, etc. Among them, pulsed laser deposition (PLD) avoids the need for post-deposition heat treatments, needed to transform undesired pyrochlore to the perovskite phase [4]. In this paper, a study is presented of the microstructural and electrical properties of composite PZT/Pt thin films that are prepared by PLD. Special attention will be paid to the influence of the Pt-phase on the film properties.

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2. Experimental

Composite PZT/Pt targets, containing Pt particles of a few μm in size, were prepared by a sol-precipitation route [3]. The Pt contents were varied from 3 to 25 vol.%. A KrF excimer laser ($\lambda = 248$ nm; pulse frequency, $f = 5$ Hz) was used to grow PZT/Pt films in an oxygen environment ($pO_2 = 0.1$ mbar) on $SrTiO_3(1\,0\,0)$ substrates. In order to have atomically flat surfaces, the substrates were chemically and thermally treated prior to deposition. In this way a TiO_2-terminated surface layer was produced [5]. The substrate temperature was kept at 600 °C to promote the crystallization of the PZT phase. The energy density *(E)* of the laser spot was 2.5 J/cm^2. The PLD-produced thin films were characterized by XRD, AFM and TEM. Their composition was determined by X-ray fluorescence (XRF). The electrical properties were evaluated using *C–V* and *I–V* measurements. Samples for the electrical characterization were prepared on single crystal Nb-doped STO substrates. The electronically conducting substrate acted as bottom electrode. The top electrode was provided by sputter deposition of gold in a surface area of 100 μm × 100 μm. The film thickness is in the range of 200–250 nm and was determined from a SEM image of the cross section.

3. Results and discussion

3.1. Microstructure

XRF analysis showed that the Pt content in the thin films is lower than in the targets. This can be explained by the energy density used (2.5 J/cm^2), which is much lower than the ablation threshold for Pt (4 J/cm^2). Higher *E* values produced films with a higher Pt content, but also caused an increased surface roughness and introduced a noticeable porosity [6]. In the following sections the indicated Pt content reflects the actual film composition, as determined by XRF.

Fig. 1 shows the XRD diagrams of a pure PZT film and PZT/Pt films with various Pt contents. All films show perovskite peaks of PZT, with a (0 0 1) preferred orientation. The presence of amorphous or pyrochlore phases could not be detected from the XRD-analysis. Pt peaks, if present, could not be identified as these overlap with STO peaks, but also because of the nanometer size of the Pt particles. The presence of a Pt-phase has been proven quantitatively by the XRF analysis, and also by TEM imaging, as shown in Fig. 2. The TEM micrograph clearly shows that the Pt particles, visible as dark spots in a bright PZT matrix phase, are dispersed homogeneously. Pt particle sizes are in the range of 3–10 nm. The PZT phase shows a columnar microstructure with an average width of 60–80 nm.

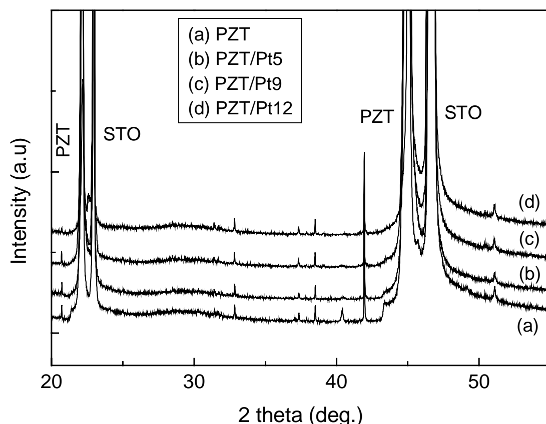

Fig. 1. XRD diagrams of PZT/Pt films with different Pt contents.

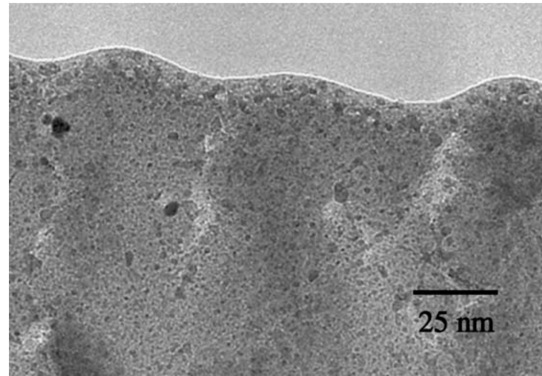

Fig. 2. TEM image of a cross section of a PZT/Pt 9 vol.% film.

The AFM pictures in Fig. 3 show that the films are relatively smooth, although the surface roughness increases with an increase in Pt content. The average particle size of PZT is around 70 nm as presented in Fig. 3a, which is in agreement with the TEM observations. In the films with higher Pt content (see Fig. 3b–c), smaller particles of 30–40 nm appear in the junctions of the larger grains. The number of these small particles in the surface increases with Pt content. It is assumed that Pt inclusions at the PZT grain junctions inhibit the growth of the PZT grains, as was also observed for bulk materials [2].

3.2. Electrical properties

C–V measurements have been carried out at room temperature at a frequency of 10 kHz. The PZT/Pt films exhibit the typical butterfly curves for ferroelectric materials, as can be seen in Fig. 4. Two maxima were observed in a retraced curve, which corresponds to the switching voltages of the internal polarization. The asymmetry and the internal bias are due to the difference in work functions between the top gold electrode and the bottom Nb-STO electrode.

The dielectric constants were calculated from the capacitance value at 0 V (before the *C–V* measurements). The dependence of the dielectric constant on Pt content is presented in Fig. 5, together with our previous result obtained on bulk PZT/Pt [3]. Increasing the Pt content results in an increase of the dielectric constant. For 12 vol.% Pt the enhancement in ε is around a factor 4 with respect to pure PZT. The much

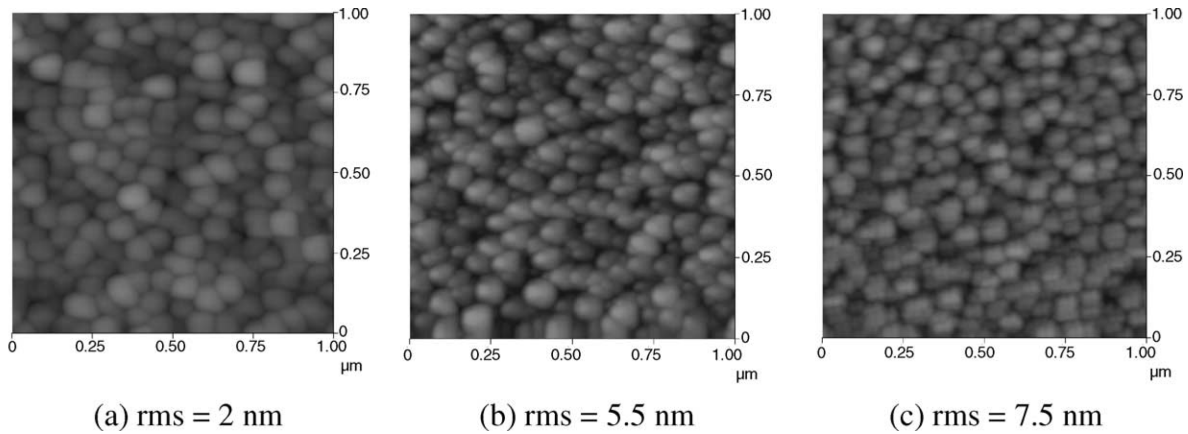

Fig. 3. AFM pictures of: (a) PZT/Pt 5 vol.%, (b) PZT/Pt 7 vol.%, (c) PZT/Pt 12 vol.% films. The root mean square surface roughness (rms) is indicated.

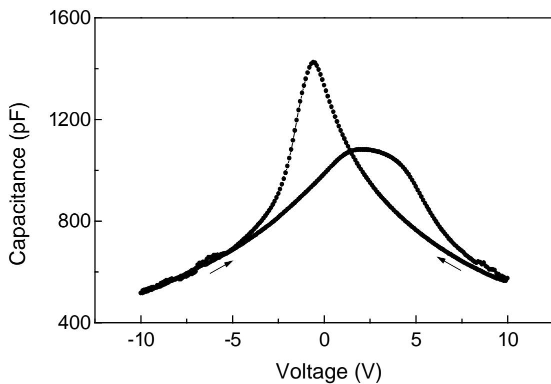

Fig. 4. C–V measurement of a PZT/Pt 7 vol.% film.

sharper increase of ε with Pt content in thin films, compared to bulk materials, is quite remarkable. It could be due to the very small size of Pt particles. Maliaris and Turner [7] have shown that the percolation threshold shifts to lower volume fractions when the particle size of the dispersed conducting phase decreases with respect to insulating phase. On the other hand, the increase in the dielectric constant can also be attributed to the space charge double layer at the PZT/Pt interfaces [8]. The interface area is in principle inversely proportional to the particle size; hence, the influence of this double layer will become more pronounced with a decrease in particle size of the dispersed phase. Further research needs to be performed in order to elucidate the origin of the enhancement in the dielectric constant.

At Pt contents higher than 7 vol.%, however, ε increases less rapidly. This may be attributed to a change in the film morphology, possibly due to a lower density of the film, smaller grain size of the matrix or a lower degree of crystallinity of the PZT phase, which is induced by the Pt addition.

In Fig. 6, the I–V characteristics measured at room temperature are presented for the pure PZT and PZT/Pt composite films. They are comprised of two main parts: the linear voltage dependent regime at low voltage and the non-linear voltage dependence at high voltage.

In the low voltage regime the Ohmic conduction dominates. The leakage current increases linearly with the voltage:

$$I = en_0\mu\frac{V}{s} \tag{1}$$

Here I is the current, e the electron charge, n_0 the free carrier density, μ the charge carrier mobility, V the applied

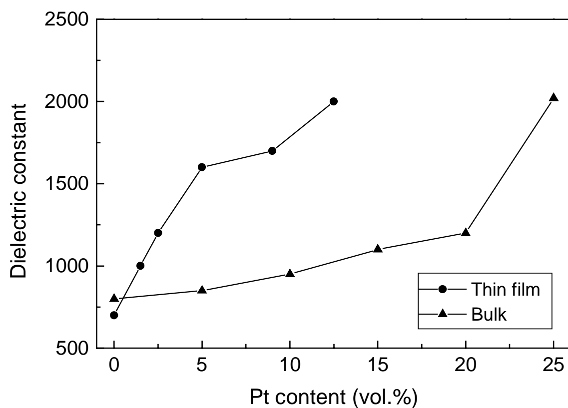

Fig. 5. Dependence of the dielectric constants on Pt content for thin films and bulk material.

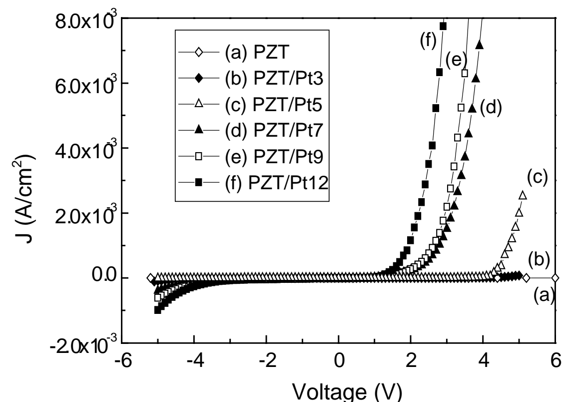

Fig. 6. I–V curves of PZT and PZT/Pt films with different Pt contents.

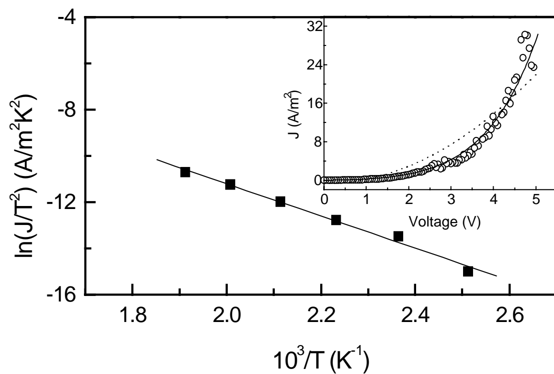

Fig. 7. Variation of $\ln(J/T^2)$ with $1/T$ for PZT/Pt 7 vol.% film. Inset: the *I–V* data measured at room temperature and model fits using Eq. (2) (dashed line) and Eq. (3) (solid line).

voltage and s the film thickness. The conduction is governed by the defect chemistry of the bulk, i.e. the type and concentration of free charge carriers [9]. At higher voltages, the conduction is governed by the injection of charge carriers at the electrode-film interface. Possible mechanisms that have been proposed for the leakage current in PZT include a space-charge-limited-current (SCLC) mechanism [10],

$$I = \frac{9}{8}k\mu\left(\frac{V}{s}\right)^2 \quad (2)$$

or thermionic Schottky emission [11,12],

$$I = A^*T^2\exp\left(-\frac{e\phi_B}{k_BT}\right)\exp\left[\frac{e}{k_BT}\left(\frac{eE}{4\pi\varepsilon}\right)^{1/2}\right] \quad (3)$$

depending on the microstructure of the film. In Eq. (3), A^* is the effective Richardson coefficient, which incorporates the carrier mobility, T the temperature, Φ_B the zero-field Schottky barrier height, k_B the Boltzmann constant and $E = V/s$ the applied electric field. Both SCLC and Schottky mechanisms can take place either successively or at the same time [13]. A Frenkel–Poole mechanism [14], a typical bulk effect, can be excluded due to the observed asymmetry in the leakage currents.

In the inset of Fig. 7, the *I–V* characteristics of a PZT/Pt 7 vol.% film were used for modeling based on Eqs. (2) and (3). Using the Schottky emission model, a good agreement between experimental data and model is obtained. From *I–V* data, measured at different temperatures, a graph of $\ln(J/T^2)$ versus $1/T$ is presented in Fig. 7. The solid line presents a linear fit to the data. From the slope of this curve the barrier height Φ_B for the PZT/Au interface can be calculated. Using Eq. (3) a value of 0.6 eV is obtained, which nicely compares with the value of 0.5 eV obtained by Waser for Ni-$SrTiO_3$/Au [15], but is distinctly smaller than 1.5 eV observed for PZT/Pt [14].

The leakage current at low voltage increases slightly with Pt content, from 2×10^{-7} A/cm^2 for a pure PZT film, to 5×10^{-6} A/cm^2 for PZT/Pt 12 vol.%. More pronounced is the shift to lower voltages of the threshold voltage, where the strong upturn in leakage current becomes apparent (Fig. 6). This can be intuitively understood if one takes into account the fact that the effective electrical field in the case of a composite thin film will be larger than simply the ratio of the applied voltage over thickness. Due to the dispersion with many conducting particles, in which there is no electrical field, the electrical field becomes redistributed across the composite thin film. Due to the increased field intensity at the interface, larger leakage currents will occur at lower applied voltages. Calculations based upon effective medium theory are in progress to support these conclusions. In this stage, however, it cannot be excluded that factors related to microstructure and/or electrode morphology play an additional role as well.

4. Summary and conclusions

PZT/Pt films prepared by PLD are epitaxial with a homogeneous dispersion of 3–10 nm Pt particles. Under the preparation conditions mentioned above, the film roughness increases with increasing Pt content. Another consequence of the increased Pt addition is the decrease in the average grain size of the PZT phase, as observed on the film surface. The explanation may be the same as for bulk material: Pt particles located at the PZT grain junctions inhibit the grain growth of PZT. Together with a lower film density, this can explain the diminished increase in the dielectric constant of composite thin films for high Pt contents. It is expected that, by optimizing the deposition conditions, the kinetics of the film growth can be controlled in a way that the effect of Pt on the crystallinity and the microstructure of PZT films can be minimized.

PZT/Pt films have a remarkably high dielectric constant when compared to pure PZT, and even to PZT/Pt bulk material with the same Pt content. The increased enhancement effect is assumed to be due to the nano-sized Pt particles.

As a side effect, the leakage current of PZT/Pt films also increases with Pt contents. It is noteworthy that the leakage current in the low voltage regime, which is governed by the bulk properties, does not change much with Pt content. The obvious change is the shifting of threshold voltage to lower values, which is governed by the electrode-film interface rather than the bulk. The most favorable mechanism for the leakage current is found to be Schottky emission, with 0.6 eV Schottky barrier height for PZT/Au.

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