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Pulsed laser deposition of PZT/Pt composite thin films with high dielectric constants

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ABSTRACT $PbZr_{0.53}Ti_{0.47}O_3$ (PZT) thin films containing nanoparticles of Pt (3–10 nm) were produced using pulsed laser deposition (PLD). The Pt content can be tuned by varying the energy density of the laser beam. Phase and microstructure analysis of the thin films was performed using XRD, SEM, TEM and AFM. The electrical properties were investigated by C–V and I–V measurements. The effective dielectric constant of the composite films increased substantially through the Pt dispersion. These films are promising candidates, for instance, for high-density dynamic random access memory (DRAM) devices.

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1 Introduction

Ferroelectric films become increasingly integrated into devices that exploit the great variety of properties exhibited by these materials, including dielectric, ferroelectric, piezoelectric, electrostrictive and pyroelectric properties. For example, high permittivity (ε) has attracted considerable interest for applications in DRAM. PZT, with an ε of 800–1000, appears to be a promising candidate for replacement of conventional SiO_2 ($\varepsilon = 3$) or Si_3N_4 ($\varepsilon = 9$) in high density DRAM [1]. The improvement in the dielectric constant of PZT-based composites through the addition of a metallic phase have been studied by a number of researchers [2–4]. Recently, we have found that ε of bulk PZT increases by a factor of four by dispersion with 25 vol. % of Pt [4], consistent with percolation theory. According to this theory, a maximum permittivity enhancement is found for concentrations of the metal phase close to the percolation threshold. Platinum was chosen since it showed no side reactions with PZT during annealing at high temperature. Preparation of the composites was carried out with the help of colloidal techniques. However, in the course of sintering the size of the Pt inclusions increased up to a few microns.

In the present paper, we report on the fabrication of PZT/Pt composite thin films using PLD. Besides the advantage of high deposition rates, high kinetic energy adatoms, most of the process parameters during PLD can be controlled independently from each other, which permits a high degree of tailoring the microstructure of the thin film. Among them, varying the laser energy density and the substrate temperature are considered to be most effective to manipulate the growth kinetics. The size and degree of dispersion of the Pt inclusions into the PZT films, and the degree of crystallization of the PZT phase have a significant influence on the permittivity. Epitaxial films are appreciated due to less grain boundaries and better films surface, leading to low leakage and better performance. The challenge in this study, therefore, lies not only in controlling the proper microstructure of PZT, but also in the heterogrowth of PZT and Pt. Preliminary results from measurements of the dielectric properties of the composite thin films with different Pt contents are presented.

2 Experimental

PZT/Pt films were grown using a KrF laser excimer ($\lambda = 248$ nm, $f = 5$ Hz) in an oxygen environment ($pO_2 = 0.1$ mbar) on $SrTiO_3(100)$ substrates. Prior to deposition, in order to have atomically flat surfaces, the substrates were chemically and thermally treated to produce a TiO_2-terminated surface layer [5]. The substrate temperature (T_s) was varied between 400 and 700 °C, the laser energy density (E) between 1.5 and 4 J/cm^2. The distance from target to substrate was changed accordingly in such a way that the substrate was located at the end of the visible laser plume. Composite PZT/Pt targets, containing Pt inclusions of a few μm in size, were prepared by a sol-precipitation route [4]. The PLD-produced thin films were characterized by X-ray diffraction (XRD), atomic force microscopy (AFM), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Their composition was determined by X-ray fluorescence (XRF). The electrical properties were evaluated using C–V (capacitance-versus-voltage) and I–V (leakage current-versus-voltage) measurements. For electrical characterization, the bottom electrode was provided by using conducting Nb-doped STO substrates. For the top electrode sputter-deposited gold was used with a surface area of 100×100 μm. The film thickness was determined from a SEM image of the cross section.

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3 Results and discussions

3.1 *Phase analysis and microstructure*

PZT/Pt films are light brown in comparison with yellowish transparent pure PZT. Deposition at higher substrate temperature leads to darker coloured films, which is tentatively explained by the increased crystallite size of the Pt particles. XRD patterns of films deposited with $E = 2.5\,\mathrm{J/cm^2}$ at different T_s using PZT/Pt 10 vol. % target are presented in Fig. 1. Besides peaks from the STO substrate, only peaks originating from PZT are observed. The absence of Pt peaks in the diagrams is possibly due to the small crystallite size (of a few nm), but also by the overlap between Pt and STO peaks. The degree of crystallization of the PZT phase evidently depends on the substrate temperature. Below 600 °C, no evidence is found for the formation of the perovskite phase of PZT. This suggests that the PZT phase exists either in amorphous or in nanocrystalline (pyrochlore) state. Only films deposited at $T_s \geq 600\,°\mathrm{C}$ show the appearance of the perovskite phase, which grows preferentially along the (100) direction. Films deposited at 700 °C show only very weak PZT lines. This may be explained by the strong re-evaporation of PbO at high temperature, leading to decomposition of the PZT phase.

AFM pictures (not presented here) provide a visualization of the change of states. The film morphology changes from extremely smooth with no grain structure (amorphous) at $T_s = 400\,°\mathrm{C}$ to an oriented fine-grained structure (nanocrystalline pyrochlore) at $T_s = 500\,°\mathrm{C}$ and finally to a globular grain structure (perovskite) with grain sizes of 60–80 nm at $T_s = 600\,°\mathrm{C}$. At the higher T_s of 700 °C, instead of a smooth surface with mono-sized grains, the films exhibit islands dispersing in a smooth matrix.

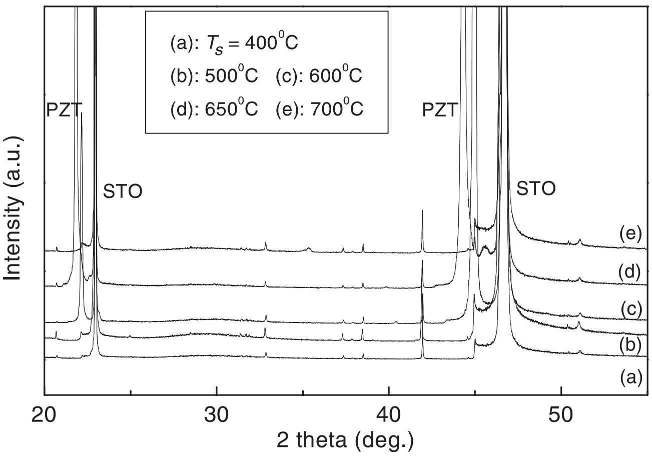

FIGURE 1 XRD patterns of films deposited at various temperatures using PZT/Pt 10 vol. % target

The dispersion of Pt inside the composite films, however, cannot be deduced from XRD and AFM analyses. Figure 2 shows a cross sectional TEM picture of a PZT/Pt film, deposited from 18 vol. % Pt target with $E = 2.5\,\mathrm{J/cm^2}$ at $T_s = 600\,°\mathrm{C}$. The film contains a columnar structure, which is in agreement with the results from XRD. The high-resolution image shows a good matching of lattice fringes between the film and the STO substrate, especially at the film–substrate interface (Fig. 2a). In an out of focus image (Fig. 2b), spherical Pt particles appeared as darker spots with respect to the PZT matrix. They are homogeneously dispersed over the film with the estimated size of 3–10 nm.

The laser energy density determines the amount of species ablated from the target and their kinetic energy; it can, therefore, strongly affect the film properties. Furthermore, the ablation threshold value of Pt is around $4\,\mathrm{J/cm^2}$ while for PZT it is only $0.3\,\mathrm{J/cm^2}$ [6], which will influence the final film composition. While using the PZT/Pt 10 vol. % target and keeping T_s at 600 °C, the energy density, E, was varied between 1.5 and $4\,\mathrm{J/cm^2}$. According to the compositional analysis by XRF, the Pt content increases with energy density (see Table 1). However at $E = 4\,\mathrm{J/cm^2}$ it still does not reach the content in the target. This can be explained by the high ablation threshold of Pt as mentioned before. XRD confirmed that within the specified range of E PZT adopts the perovskite structure. Of interest is the drastic change in film morphology, as shown in Fig. 3.

A clear grain structure was observed for all films deposited at $E > 2\,\mathrm{J/cm^2}$ (Fig. 3b–c). The surface roughness increases strongly with energy density. For films deposited at $E = 4\,\mathrm{J/cm^2}$, the grains have inhomogeneous size and irregular shapes (Fig. 3c). Smaller grains appear in comparison with those of films deposited at $E = 2.5\,\mathrm{J/cm^2}$. Most surprisingly is that an extremely smooth surface, which follows the steps of the underlying substrate, even at a thickness of 100 nm, is

E (J/cm^2)	1.5	2.5	3.5	4
vol. % Pt	3.6	4.1	4.5	4.9

TABLE 1 Pt content in the composite thin film as a function of energy density, obtained for PZT/Pt 10 vol. % target

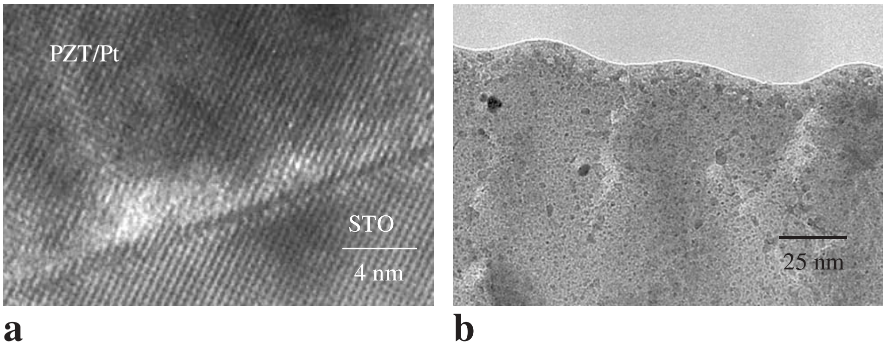

FIGURE 2 TEM image of film deposited from PZT/Pt 18 vol. % target

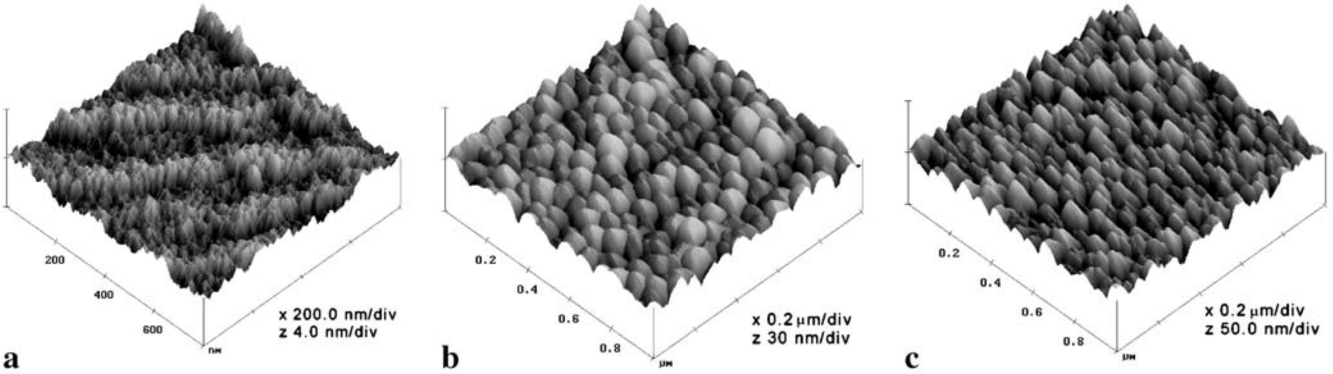

FIGURE 3 3D-AFM images of films deposited from PZT/Pt 10 vol. % target at different energy densities: 1.5 J/cm^2 (**a**), 2.5 J/cm^2 (**b**), 4 J/cm^2 (**c**)

obtained at $E = 1.5\,\mathrm{J/cm^2}$ (Fig. 3a). One would expect that higher energy densities produce a smoother film surface, as the adatoms will have more kinetic energy to diffuse along the surface but not stick on top of each other. An opposite trend, however, is observed in our case. Hence, besides the kinetic energy of incident atoms, other factors that control the growth mechanism of the film need to be considered. The first one might be the arrival rate of adatoms to the substrate, being proportional to the energy density. Too high an arrival rate will limit the time for adatoms to diffuse along the surface. Higher arrival rates and higher density of adatoms also create more nucleation sites, explaining the smaller grain size observed at $E = 4\,\mathrm{J/cm^2}$. The interfacial free energy between the Pt and PZT phases is possibly another factor that influences the heterogrowth of PZT/Pt composite layer. The non-wetting behavior of Pt towards PZT may favor that Pt is situated on top of existed PZT islands rather than to diffuse to the edge of the islands. As revealed by XRF, the Pt content in composite films increases with energy density, which increasingly facilitates the island growth. Also of importance is the formation of particulates during PLD, especially for materials containing volatile components such as Pb [6]. High energy densities produce more particulates with larger sizes, which strongly increase the roughness of the film.

3.2 *Electrical properties*

The dielectric constant of the composite films can be calculated from the capacitance values at 0.5 V, taken from a C–V measurement, using the following equation: $\varepsilon = Ct/\varepsilon_0 A$ where C is the capacitance, t is the thickness of the film, A is the electrode area and ε_0 is the permittivity of the vacuum. Table 2 lists ε-values of PZT/Pt films deposited from targets with different Pt contents. Films were deposited with $E = 2.5\,\mathrm{J/cm^2}$ at $T_s = 600\,°\mathrm{C}$ for 15 min. When compared with pure PZT, ε increases with a factor of 1.5 for 3 vol. % Pt and about a factor of three for 10 vol. % Pt. The leakage current also increases with Pt content, but remain acceptably low ($< 10^{-6}\,\mathrm{A/cm^2}$) for DRAM application.

The increase in the dielectric constant can be explained qualitatively as follows. The dispersed Pt particles form conducting clusters that stretch across the insulating host. Each pair of clusters, separated by a thin dielectric region, creates a capacitance. Those capacitances are parallel and can contribute an anomalous value, depending on the effective surface area of the metal clusters and the thickness of the dielectric layer. A large electric field in the thin insulating regions is also responsible for an increase in the dielectric constant [7]. Quantitatively, it can be explained by percolation theory, which predicts that the dielectric constant of a metal-insulator mixture diverges near a critical volume fraction of the metal, called the percolation threshold [8]. Further studies will be carried out.

vol. % Pt	0	3	5	10
ε	700	1000	1250	1900

TABLE 2 Dielectric constants of PZT/Pt films

4 Conclusions

Nano-composite PZT/Pt thin films were prepared by PLD from composite targets. The deposition temperature is very crucial for crystallization of PZT. The PZT matrix transforms from amorphous to nanocrystalline pyrochlore to globular grain-structured perovskite with an increase of the deposition temperature within range from 400 to 600 °C. An epitaxial film was obtained in a limited deposition temperature range from 600 to 650 °C. At those temperatures, films grow in columns, with a homogenous dispersion of Pt particles 3–10 nm in size. A higher temperature of 700 °C, however, does not improve the crystallinity, but rather decomposes the PZT phase due to strong PbO re-evaporation at high temperature. The energy density significantly influences the film properties. A high energy density favors the ablation of Pt and, therefore, leads to a higher Pt content in the film. Additionally, the film roughness increases with increasing energy density. Dispersing Pt in PZT significantly enhances the dielectric constant, from 700 for pure PZT to 1900 for the composite deposited from 10 vol. % Pt target.

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