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Piezoelectric properties of epitaxial Pb(Zr$_{0.525}$, Ti$_{0.475}$)O$_3$ films on amorphous magnetic metal substrates

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Epitaxial growth of high piezoelectric constant Pb(Zr$_{0.525}$, Ti$_{0.475}$)O$_3$ (PZT) thin films deposited on amorphous magnetic Metglas® substrates by pulsed laser deposition (PLD) is reported. Particularly, Pt or Au buffer layers were employed to initiate epitaxial growth of the PZT films from atop of an amorphous surface. The optimization of deposition conditions for the PZT films with different buffer layers was systematically investigated. The crystal structure, texturing, and surface morphology of the samples were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). Ferroelectric and piezoelectric properties were measured indicating high polarization 27 μC/cm^2 and piezoelectric constant d_{33}, 46 pm/V for the Pt buffered films. The PZT thin films grown on a magnetostrictive material have demonstrated high quality crystallographic structure and piezoelectric response, having potential for use in emerging magnetoelectric sensors. © 2012 American Institute of Physics. [doi:10.1063/1.3677864]

I. INTRODUCTION

Among the properties of ferroelectrics that are of renewed interest are those with potential application in multiferroic structures for applications that include magnetic field sensors, tunable phase shifters and filters, energy harvesting, etc. The magnetoelectic (ME) effect enables electric polarization from the application of magnetic fields, and vice versa.[1–3] One such ferroelectric, Pb(Zr$_{0.525}$, Ti$_{0.475}$)O$_3$, or PZT,[4] plays an important role in many magnetoelectric heterostructures. A large ME coupling in the heterostructure is determined by the selection of magnetostrictive and piezoelectric materials. Obviously, a high magnetostrictive coefficient and/or piezoelectric constant is required. The amorphous magnetic material, Metglas®,[5] is often employed to construct a ME heterostructure because of its high megnetostrictive coefficient and ultra-soft magnetic properties. More importantly, Metglas® shows a maximum value of the piezomagnetic coefficient at a very low bias magnetic field ($\sim$10-20 Oe), which is of great significance to the designs of ME sensors requiring high sensitivity, low biased field operation, and low power consumption.[6] Additionally, its unique properties, such as flexibility, ductility, and high permeability are quite attractive. It is pointed out that the remarkable performance of Metglas® benefits from the nature of the amorphous structure. One of the biggest challenges in constructing Metglas®-based PZT film heterostructures is how one retains the amorphous state of while experiencing a thermal anneal during processing that approaches 400–700 °C.

In this work, we successfully demonstrate the growth of PZT films on a Metglas® substrate by pulsed laser deposition (PLD).[7,8] The growth depends upon the selection of a buffer layer (i.e., Pt or Au) between Metglas® and PZT. We address here the effects of the buffer layer on epitaxial growth, crystallographic texturing, ferroelectric, and piezoelectric properties, etc. for the PZT films with thicknesses ranging from 2.1 to 2.4 μm. It was found that the (111) orientation PZT thin films were deposited with high crystal quality on either Pt or Au buffered substrate, while the thin films with a Pt layer exhibited a higher polarization and piezoelectric constant.

II. EXPERIMENT

Metglas® substrates were buffered with Pt or Au layers to form a seed layer for the epitaxial growth of PZT films. Pt and Au facilitate epitaxy because they possess crystal structures and lattice parameters similar to PZT. The seed layers, deposited using DC magnetron sputter deposition, had (111) orientation and thicknesses of 80–150 nm. PLD was employed to deposit PZT at a temperature of 650 °C under varying oxygen pressures. Two pieces of Metglas® substrates, buffered with Pt or Au, were mounted on the substrate holder for each deposition cycle. The effect of oxygen pressure on the growth was investigated for deposition time of 3.5 h under 100, 150, and 200 mTorr, respectively. By using a profilometer, the thicknesses of the samples were determined to be 2.1–2.4 μm. The crystal structure was characterized by X-ray diffraction (XRD) indicating a single phase PZT structure existed when the deposition operated at 650 °C with O$_2$ pressure from 100 to 200 mTorr. Scanning electron microscopy (SEM) was utilized to capture surface images of the PZT films. Chemical compositions were also determined by energy-dispersive

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X-ray spectroscopy (EDX), yielding the ratio of Pb: Zr: Ti, (1-1.15): 0.52: (0.44-0.48). The ferroelectric properties were measured by polarization hysteresis measurement driven by a triangular waveform of 10 kHz frequency. The piezoelectric coefficient d_{33} was measured by using Veeco SPI 3100 piezoelectric force microscopy (PFM).

III. RESULTS AND DISCUSSION

XRD spectra for the PZT films deposited on Metglas® substrates with either Pt or Au as a buffer layer were collected. The XRD patterns obtained for the Pt buffered samples are presented in Fig. 1(a) for different oxygen pressure depositions. It is noticed that the PZT films remain as a pure phase structure as the oxygen pressure changes from 100 to 200 mTorr. The peaks at 31.2° and 38.3° correspond to (110) and (111) planes of the PZT film, respectively. It is clear that the (111) plane is dominant. The (111) plane of the Pt or Au buffer layer should be at $2\theta = 39.5°$ and 38.1°, respectively. But, it is invisible for Au buffered films because the Au (111) peak overlapped the PZT (111) peak, as shown in Fig. 1(b). At an oxygen pressure of 100-200 mTorr, the PZT crystal film is strongly orientated along the ⟨111⟩ direction as determined by the templating by the Pt or Au (111) oriented buffer layers. With the variation of oxygen pressure, either Pt or Au buffered PZT film presents similar trends in growth, i.e., the PZT films are of (111) preferable orientation that is manipulated by the (111)-oriented Pt or Au buffer layer. It builds up a solid foundation for an enhancement of the ferroelelctric and piezoelectric performance.

The surface morphology of PZT films on Metglas® substrates were observed by SEM, as shown in Fig. 2. The SEM images represent the PZT films deposited at 650 °C and under 100 mTorr, 150 mTorr, and 200 mTorr O_2 pressure with Pt or Au buffer layer, respectively. The SEM images of the PZT
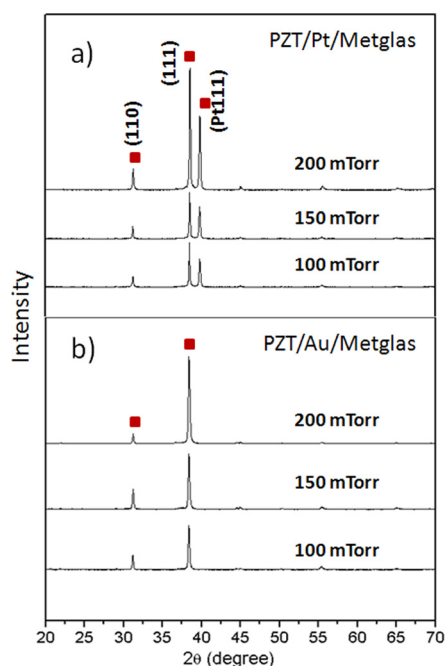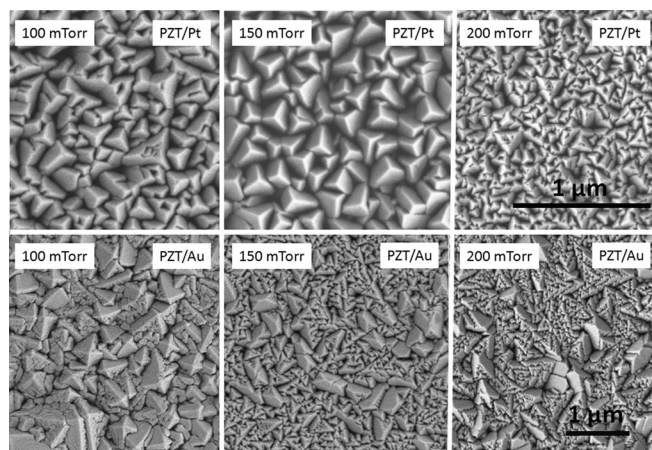

FIG. 2. SEM images of Pt or Au buffered PZT thin films under different oxygen pressures.

films with a Pt buffer layer resulted in very uniform grain growth with triangle-shaped grains, reflecting strong (111) orientation. However, Au buffered films showed somewhat an inhomogeneous and non-uniform distribution of the grains. Some of the grains for the Au buffered PZT thin film look like octahedral shaped agglomerations containing triangle-shaped fine grains. It implies that the growth of PZT crystal is incomplete, which is quite different from the growth on the Pt buffer layers. The difference in morphology between Au and Pt buffered PZT films may arise from different lattice mismatches and/or roughness of the buffer layer. Note, that the lattice constant of the Pt, Au, and PZT crystals is 3.920, 4.080, and 4.040 Å, respectively. Bragg equation and Miller indices were used to calculate lattice constants for both Pt and Au buffered. The PZT was considered to be a tetragonal structure, and lattice constant a and c are listed in Table I.

It was found the PZT deposited on an Au buffered layer had a larger lattice constant a than that deposited on Pt buffered. That is, the lattice constant of PZT buffered with Au is closer to the Au lattice constant (4.08 Å). As the pressure rises, the c/a ratio increases gradually for both Pt and Au buffered PZT films, indicating a slight change in the PZT crystal from cubic to tetragonal symmetry. A small lattice mismatch is responsible for continuous and rapid growth of the PZT crystal structure. Note that by reducing the oxygen pressure from 200 to 100 mTorr,[9] either Pt or Au buffered PZT thin film tends to form the microstructure with fine grains. Actually, as the pressure is reduced, the surface mobility increases, creating larger grains. When the pressure is reduced, the free mean path is increased, resulting in the reduction of thermalizing collisions of particles during a deposition process. With fewer thermalizing collisions the adatom mobilities remain high, resulting in larger grains and thicker films (i.e., deposition rates).

It is clear to see from the SEM images that both Pt and Au buffered PZT films show similar behavior in response to the changes in deposition pressure, that is, the grain size increases as the oxygen pressure decreases.

More importantly, ferroelectric measurements of the PZT films were performed, i.e., piezoelectric constant d_{33} and polarization hysteresis loop.[10] Fig. 3(a) is a representative ferroelectric hysteresis loop with an applied voltage of 50 V s for both Pt

FIG. 1. (Color online) XRD pattern of PZT thin film on Pt (a) and Au (b) buffer layer.

TABLE I. Comparison of PZT lattice constant between Pt and Au buffered samples by using XRD analysis.

O$_2$ Pressure (mTorr)	Lattice constant (Å) of PZT with Pt buffer layer			Lattice constant (Å) of PZT with Au buffer layer		
	A	c	c/a	a	c	c/a
100	4.0509	4.0787	1.0069	4.0540	4.0580	1.0010
150	4.0472	4.0909	1.0108	4.0483	4.0877	1.0097
200	4.0444	4.2665	1.0549	4.0460	4.2953	1.0616

and Au buffered PZT samples grown at 650 °C under 150 mTorr oxygen pressure. For Pt buffered sample, it is found that the saturation polarization and a remnant polarization are $P_s \approx$ 27 μC/cm^2, and $P_r \approx$ 10 μC/cm^2, respectively. While the Au sputtered PZT film has $P_s \approx$ 16 μC/cm^2 and $P_r \approx$ 6 μC/cm^2. Obviously, Pt buffered PZT films show higher polarization than that of Au buffered films, which resulted from the uniform and continuous growth of films with fine grains on a Pt buffered substrate. Nevertheless, those values for both of the films are comparable to other PZT films previously reported.[11,12] Since the Pt buffered PZT film has a slow deposition rate, compared to the Au buffered one, it leads to a thinner PZT layer, corresponding to a high coercive field.[13] It is assumed that the microstructure with fine grains in the Pt buffered PZT films may offer large permittivity due to high grain boundary capacitance, consequently resulting in a high saturation polarization. Also, from the previous SEM images, it is clear that the PZT thin film with an Au layer reveals non-uniform surface so as to generate an extra leakage current which may reduce the ferroelectric polarization.

Finally, the piezoelectric constant d_{33} was measured as a function of applied voltage, as shown in Fig. 3(b). The curve from Pt buffered layer presents a more symmetric butterfly shaped loop and a higher d_{33} value, than those of Au buffered PZT films. The measurement indicates a maximum value of $d_{33} \sim$ 46 pm/V of the Pt buffered sample, and 35 pm/V of the Au buffered one. The $d_{33} \sim$ 46 pm/V of the Pt buffered sample is 53% higher than the reported piezoelectric constant d_{33} of

BTO deposited on Metglas® substrate.[14] Such a high d_{33} may benefit from three factors: (1) the uniformity of the structure provides a better strain transfer,[15] (2) the PZT film is of high quality in crystallography, and (3) Metglas® might provide smaller strain inside PZT film than Si substrates. The magnetic properties of the raw Metglas® and annealed substrate were measured by a vibrating sample magnetometer (VSM) at room temperature, shown in Fig. 3(c). The raw Metglas® presents a saturation field of 400 Oe and saturation magnetization ($4\pi M_s$) of 16.3 kG, whereas the annealed one requires higher saturation field of 800 Oe and shows slight reduction in $4\pi M_s$ (15.8 kG). However, an increase in coercive field is measured because of high temperature annealing. The slight degradation in magnetic properties is attributed to somewhat crystallization of the amorphous alloy. Nevertheless, the substrate is still suggested to have potential to the demonstration of large ME coupling.

IV. CONCLUSIONS

PZT thin films were epitaxially grown on Metglas® substrates with Pt or Au buffer layers by PLD at 650 °C under oxygen pressures of 100, 150, and 200 mTorr. The crystal structures were confirmed by XRD and the SEM measurements indicate samples with Pt buffered provide more uniform surface morphology. With pressure increases, smaller grain size particles were observed for both Au and Pt buffered films. When investigating piezoelectric constant d_{33} and polarization hysteresis loop, the PZT thin films with a Pt buffer layer display higher ferroelectric response and piezoelectric properties, than Au buffered films. This study offers an approach to growing textured piezoelectric PZT oxide films on an amorphous Metglas® alloy, which may open a new pathway for demonstration of the ME-based magnetic sensors by means of strong coupling between PZT and Metglas®.

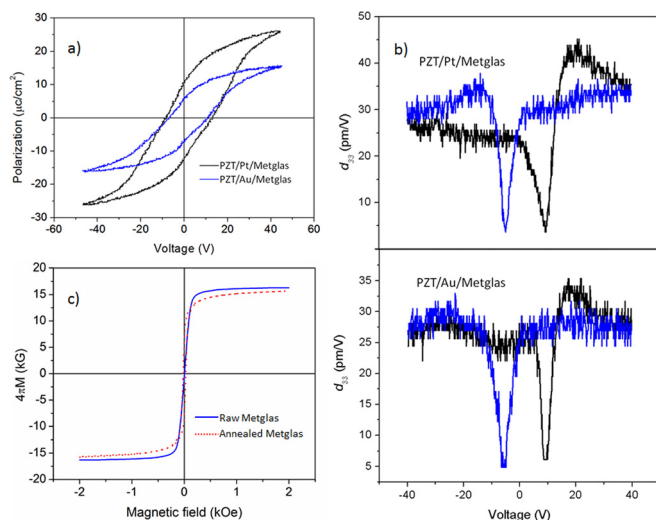FIG. 3. (Color online) (a) Ferroelectric measurements for PZT thin films on a Metglas® substrate with an Au or Pt buffer layer. (b) Piezoelectric coefficient d_{33} measurements for the PZT thin film on a Metglas® substrate with a Pt or Au buffer layer. (c) Magnetic properties of Metglas® with PZT grown on top.

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