ANTIFERROELECTRIC TO PARAELECTRIC PHASE TRANSITION IN LEAD ZIRCONATE THIN FILMS

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ABSTRACT

Lead zirconate, $PbZrO_3$, is antiferroelectric at room temperature and has a first-order phase transition to the paraelectric state at 230°C in bulk crystals. At room temperature, the antiferroelectric Pb displacements along [110] directions produce a superstructure at the (h+¼, k+¼, l) positions (referenced to pseudo-tetragonal unit cell). The Pb displacements occur perpendicular to the shorter *c* axis. In this study, the behavior of thin films was compared to the bulk. Films of lead zirconate were deposited onto electroded silicon wafers via the sol gel method. By varying the deposition conditions of the Pt substrate, films with both {111} and {100} preferred orientation were grown. The crystalline film consisted of columnar grains which were not completely aligned with each other, but had a random orientation with respect to the film's perpendicular axis. Measurements of superstructure peak intensities vs. temperature show that the thin films exhibit a much more gradual phase transition to the paraelectric state compared to the bulk. Furthermore, comparison of *a* and *c* vs. temperature show this effect, as well as a strain of about 0.5% in *c*. In the {100} oriented films, we found that the *c*-axis was oriented perpendicular to the film's surface, meaning they should be classified as (001).

INTRODUCTION

Lead zirconate, $PbZrO_3$, is an antiferroelectric material at room temperature and belongs to the perovskite class. It is best known as one of the endpoints in the technologically important class of materials comprised of $Pb(Zr_{1-x}Ti_x)O_3$. The basic structure of lead zirconate, or PZ, is pseudo-tetragonal and consists of Pb atoms on the perovskite cube corners, Zr atoms in the body center, and O atoms on the body faces. A pattern of alternating Pb displacements along the [110] directions gives PZ its antiferroelectric character (Figure 1) and defines the ab plane. The shorter *c*-axis points out of the page. As temperature is increased past its Curie temperature (T_C) of 230°C, PZ goes through a first-order phase transition to the paraelectric cubic state and the Pb displacements disappear. Also, a ferroelectric state can be induced below T_C through application of an electric field. These phase transformations cause strains to develop as the structure changes, and may lead to applications of PZ or related materials as thin-layer actuators.

At room temperature, lead zirconate has the space group Pbam and is very nearly tetragonal with lattice constants of $a = 4.153$ Å and $c = 4.101$ Å (1). The pattern of alternating Pb displacements is shown in Figure 1, which depicts the proper orthorhombic unit cell on top of the pseudo-tetragonal one.

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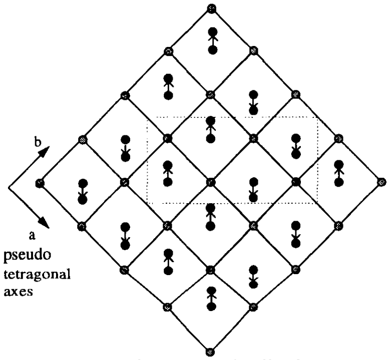

Figure 1. Antiferroelectric displacements of the Pb atoms result in an expanded orthorhombic unit cell. Pb shown in body centers (c=0.5). Zr on corners (c=0).

Thin films of PZ were grown on electroded silicon wafers with both {100} and {111} preferred orientations. Our goal was to study the phase transitions of these films and compare them to bulk crystals. We also studied the structural properties of PZ at room temperature to see what effect the substrate had on domain size and preferential orientation of the *c*-axis.

EXPERIMENT

Growth

Lead zirconate films with thicknesses of ~ 4000 Å were deposited by a chemical solution sol gel process. The method is described in more detail by Tani, et al (2). The substrate base was a {100}-oriented silicon wafer covered by a layer of SiO_2. Layers of polycrystalline Ti and Pt formed an electrode. Because the PZ films were grown on this substrate, crystalline epitaxy never could occur. Preferential {111} orientation was achieved by depositing a thin layer of TiO_2, so the entire substrate consisted of: TiO_2/Pt/Ti/ SiO_2/Si. Formation of Pt_3Ti encouraged growth of {111} domains. Self-textured growth of crystals with preferred {100} orientations was obtained on Ti free surfaces, in accordance with minimum surface energy conditions for flat-faced surfaces. Partially hydrolyzed lead zirconate solutions were deposited on the substrates by spin casting at 3000 rpm. Eight to ten layers of the PZ precursor solution were deposited, topped by a PbO layer to prevent pyrochlore formation. Crystallization occurred by heating to 700°C for 1-5 minutes. Strong {111} oriented films were grown easily on the TiO_2 modified electrodes. The strongest {100} oriented films were grown with aged solutions, indicating Pb-deficient conditions favor {100} growth.

X-ray diffraction

Measurements were taken at Brookhaven National Laboratory's National Synchrotron Light Source on Beamline X16C. The incoming X-ray beam was tuned to 10.0 keV and focused onto the center of the lead zirconate film. The film was placed with its surface aligned perpendicular to the phi axis. For diffraction measurements, this direction was also defined as the Miller index l. Because of the fiber texture, off-specular reflections and the weak superstructure reflections required synchrotron radiation to get an appreciable signal.

Because the PZ films were grown on polycrystalline platinum electrodes, the various grains were not completely aligned. The substrate allowed the thin films to attach with any orientation with respect to an axis perpendicular to the film (phi axis). As a result, the crystallographic peaks lie in rings around the axis of the surface normal, and the diffraction pattern has 'fiber texture.' This lowers the number of degrees of freedom in the experiment and makes it harder to extract precise crystallographic information. It also has the effect of making some bulk reflections appear quite close to superstructure peaks, but not as badly as in a powder sample.

To further complicate matters, the crystallized grains were also slightly tilted by varying amounts with respect to the surface of the film. This was most likely due to the faceting and non-uniform surface of the polycrystalline Pt electrode. This caused the peaks to be broad in the transverse direction. Fortunately, the range of orientations was limited to about 10 degrees, thus distinguishing the 'semi-crystalline' films from a complete powder.

At least two bulk reflections were measured in order to orient the crystal in the diffractometer. Radial scans (θ-2θ) were used to determine lattice constants, tetragonal splitting, superstructure peak intensities and information on the size and shape of domains. For the temperature studies, an evacuated chamber was mounted on the diffractometer. A cartridge heater was mounted inside a specially designed sample holder and was capable of heating the sample to 235°C.

RESULTS

Structural studies

For the preferentially {100} oriented film ('PZ100'), we found that the films grew almost entirely with their *c* axis oriented perpendicular to the substrate. Since the tetragonal phase is almost cubic, this was best seen by measuring the difference between the (002) and (200) peak positions. The (200) reflection was grazing incidence and hence gave the lattice spacing of planes perpendicular to the film. The (002) was normal incidence and gave the spacing of planes parallel to the film. At room temperature, we found the (002) at 4.114 Å (*c*) and the (200) at 4.153 Å (*a*). In the (002) measurement, very little contribution at the (200) spacing was detected (and vice versa), indicating that most of the domains were oriented with their *c* axis perpendicular to the film, making it a (001) film.

The preferred *c*-axis direction was confirmed in superstructure peak measurements. Since the Pb displacements occur within the a [110] plane, they produce superstructure peaks at the (h+¼, k+¼, l) positions, where h, k and l are integers and can be permuted. The *c*-axis orientation of a particular domain defines which of h, k and l remains an integer. We observed that reflections of the (h+¼, k+¼, l) variety gave about 10 times the intensity of a (h, k+¼, l +¼) type peak, indicating again that the crystals mainly chose their *c*-axis perpendicular to the film (the l direction). This was surprising because the lattice constant of Pt is about 5% smaller than PZ, so one might expect the smaller *c*-axis to align parallel to the substrate.

For the films with their (111) axis perpendicular to the film ('PZ111'), there are 3 equivalent (100) directions for the crystals to choose a *c* axis. Hence, we found no preferred *c*-axis direction. Contributions from the different domains caused reflections such as (200) and (002) to occur next to each other, resulting in a split peak. At room temperature, the lattice constants were: a = 4.158 Å and c = 4.123 Å. Compared to the bulk values, *c* is strained by 0.5%.

The structure of these thin films and the size of the Pb displacements can be determined by the analysis of several superstructure peaks, and will be discussed in a future paper.

Temperature studies

The integrated intensity of the (0.25, 0.75, 1) superstructure peak was measured as a function of temperature for both PZ100 and PZ111 (Figure 2). Their intensities gradually diminished until disappearing at about 220°C in the {111} oriented films and 225°C in

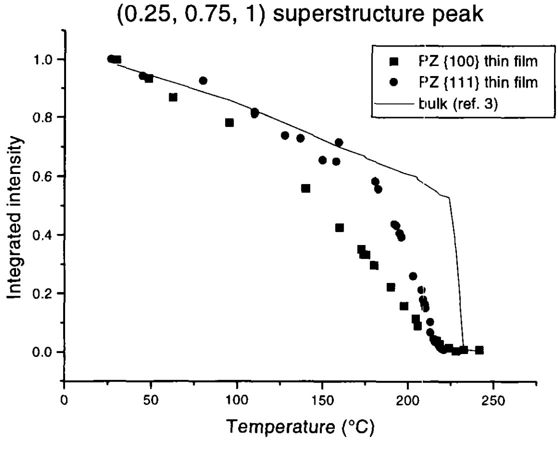

Figure 2. Comparison of superstructure peak intensity in {100} films, {111} films and bulk crystals.

the {100} films. This is in contrast to the bulk crystal behavior where the phase transition is definitely first-order and occurs at 232°C on heating and 229°C on cooling (3). At the level of temperature accuracy, our data do not show such a hysteresis, but we did observe the peak was slightly weaker and broader after annealing, suggesting a permanent rearrangement of antiferroelectric domains. It is also interesting that the PZ100 film shows a more gradual transition than PZ111. In dielectric studies (2), PZ111 films were found to be of higher quality, or more bulk-like, with a 33% greater polarization saturation value.

The temperature dependence of the lattice constants, *a* and *c*, are shown in Figures 3 and 4 for PZ100 and PZ111. Again we see that the transition is not as sharp as the bulk data measured by Sawaguchi (1). The data for PZ111 were taken from the splitting of the (200) peak, while the data for PZ100 were derived from the (200) and (002) peak

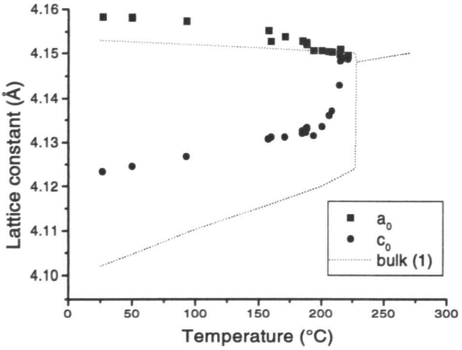

Figure 3. *a* and *c* vs. Temperature for (001) oriented film.

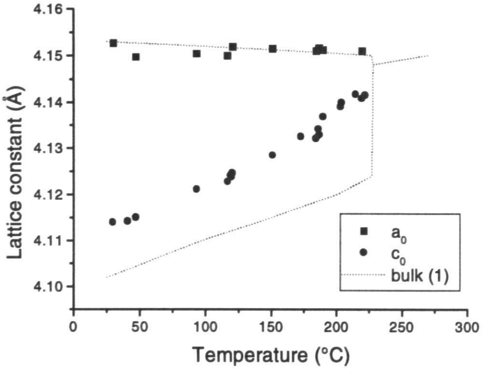

Figure 4. *a* and *c* vs. Temperature for {111} oriented film .

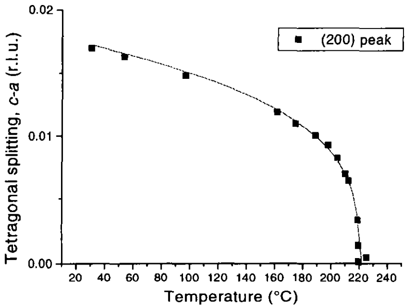

Figure 5. Fit of tetragonal splitting in PZ111 to power law.

positions. The tetragonal splitting of the PZ111 data was fit to a power law:

$$I = I_0\left(1 - \frac{T}{T_C}\right)^x$$

resulting in an exponent $x = 0.30 \pm 0.03$ and Curie temperature of 220±1 °C (Figure 5).

CONCLUSIONS

Any structural phase transition whose order parameter couples to the lattice parameter is expected to have its behavior modified when attached to a substrate because of interfacial stress. Most significantly, the first-order bulk phase transition could be changed to higher order. In the bulk, at least two structures (e.g., displacement of the Pb atoms and rotation of the oxygen octahedra) compete for the lowest energy and switch at the phase transition which is usually first-order. Our main result is that the transition in the thin film appears to be second order or higher. Two different aspects of the order parameter were probed in these experiments: the intensity due to the antiferroelectric Pb displacements and the lattice parameters. It is even conceivable that there are two independent order parameters, although our data are inconclusive. Another related possibility is that the more gradual phase transition in the thin film is simply due to common surface effects whereby the structure is modified over some depth from the periphery of each grain.

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