

Preparation and Characterization of Lead Zirconate Thin Films by Chemical Solution Deposition

X. G. Tang,^{*,†} A. L. Ding,[†] Y. Ye,[†] and H. L. W. Chan[‡]

Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, People's Republic of China, and Department of Applied Physics and Materials Research Centre, The Hong Kong Polytechnic University, Kowloon, Hong Kong, China

Received October 1, 2001. Revised Manuscript Received March 5, 2002

Lead zirconate (PbZrO₃) thin films were grown on platinum-coated silicon substrates by a chemical solution deposition. The precursor solution for spin-coating was prepared from lead acetate trihydrate and zirconium oxynitrate dihydrate as starting materials and 2-methoxyethanol as solvent; the perovskite PbZrO₃ thin films have been obtained. Atomic force microscopy (AFM) reveals that the surface morphology smooth, and the average grain size is about 180 nm. The PbZrO₃ thin films annealed at 650 °C showed a hysteresis loop at an applied electric field of 600 kV/cm with remanent polarization (P_r) and coercive electric field (E_c) electric values were 7.4 $\mu\text{C}/\text{cm}^2$ and 210 kV/cm, respectively. At 100 kHz, the dielectric constant and dissipation factor of PbZrO₃ film are 300 and 0.020, respectively. The refractive index n and the extinction coefficient k of the PbZrO₃ thin films were obtained by spectroscopic ellipsometry (SE) as a function of the wavelength in rang from 345 to 1700 nm. At 633 nm, the refractive index n and extinction coefficient k were 2.236 and 0.0474, respectively.

Introduction

Ferroelectric thin films have received increasing attention because of their application in dynamic random access memories, nonvolatile random access memories, high-frequency transducers, high value capacitors, solid-state displays, and infrared detectors.^{1,2} A particularly large volume of research has been devoted to ferroelectric thin films with the perovskite structure, such as BaTiO₃,³ PbTiO₃,⁴ Pb(Zr,Ti)O₃ (PZT),^{5–7} (Ba,Sr)-TiO₃,⁸ (Pb,Ca)TiO₃,⁹ etc. PbZrO₃ is the most extensively studied antiferroelectric material. In the past decade, there have also been a few reported on thin films of antiferroelectric materials such as PbZrO₃, which have potential applications in phase switching, charge storage, current sources, and linear capacitors. They can also be used in microelectronic or microelectromechanical devices. The preparation of PbZrO₃ thin films was first reported by Budd et al.,¹⁰ they observed those sol-

gel-derived PbZrO₃ films were more susceptible to cracking and resistant to crystallization than PbTiO₃ or PZT films. Wang et al.¹¹ reported the preparation of acetate-processor-derived films; the improved dielectric strength of these PbZrO₃ thin films allowed for the attainment of field levels necessary to observe the antiferroelectric to ferroelectric transformation at room temperature. Bai et al.¹² reported the preparation of epitaxial PbZrO₃ films on SrTiO₃ substrates by metal-organic chemical vapor deposition. Chattopadhyay et al.¹³ reported the preparation of *c*-axis-oriented PbZrO₃ layer on Si substrates by pulsed laser ablation. Tani et al.¹⁴ reported piezoelectric results for sol-gel-derived PbZrO₃ thin films.

PbZrO₃ films have been prepared successfully via the sol-gel process, using a variety of precursors.^{10–12,14} Usually, metal alkoxides (including lead alkoxide) are used to prepare the PbZrO₃ films. However, these metal alkoxides are generally expensive and are well-known for their high sensitivity to moisture. Therefore, the handling of these materials and the coating process must be conducted in a dry atmosphere. Recently, some literature reported the preparation of PZT films by use of zirconium oxynitrate or zirconium nitrate as the zirconium source.¹⁵ In this work, we use zirconium

* Corresponding author: e-mail xgtang6@yahoo.com; Fax +86-21-62513903.

[†] Chinese Academy of Sciences.

[‡] The Hong Kong Polytechnic University.

(1) Polla, D. L.; Francis, L. F. *Annu. Rev. Mater. Sci.* **1998**, *28*, 563.
(2) Kingon, A. I.; Streiffer, S. K.; Baseri, C.; Summerfelt, S. R. *MRS Bull.* **1996**, *21* (7), 46.

(3) Wu, Z.; Kumagai, N.; Yoshimura, M. *Chem. Mater.* **2000**, *12*, 3356.

(4) Lai, Y. C.; Lin, J.-C.; Lee, C. *Appl. Surf. Sci.* **1998**, *125*, 51.
(5) Chen, I.-S.; Roeder, J. F.; Glassman, T. E.; Baum, T. H. *Chem. Mater.* **1999**, *11*, 209.

(6) Scott, J. F.; Paz de Araujo, C. A. *Science* **1989**, *246*, 1400.
(7) Tohge, N.; Takahashi, S.; Minami, T. *J. Am. Ceram. Soc.* **1991**, *74*, 67.

(8) Huang, Z.; Zhang, Q.; Whatmore, R. W. *J. Appl. Phys.* **1999**, *85*, 7355.

(9) (a) Sirera, R.; Leinen, D.; Rodriguez-Castellon, E.; Calzada, M. L. *Chem. Mater.* **1999**, *11*, 3437. (b) Tang, X. G.; Zhou, Q. F.; Zhang, J. X. *Thin Solid Films* **2000**, *375*, 159.

(10) Budd, K. D.; Dey, S. K.; Payne, D. A. *Br. Ceram. Soc. Proc.* **1985**, *36*, 107.

(11) (a) Wang, F.; Li, K. K.; Haeertling, G. H. *Opt. Lett.* **1992**, *17*, 1122. (b) Li, K. K.; Wang, F.; Haeertling, G. H. *J. Mater. Sci.* **1995**, *30*, 1386.

(12) Bai, G. R.; Chang, H. L. M.; Lam, D. J.; Gao, Y. *Appl. Phys. Lett.* **1993**, *62*, 1754.

(13) Chattopadhyay, S.; Ayyub, P.; Pakar, V. R.; Muttani, M. S.; Pai, S. P.; Purandare, S. C.; Pinto, R. *J. Appl. Phys.* **1998**, *83*, 7808.

(14) Tani, T.; Li, J.-F.; Viehland, D.; Payne, D. A. *J. Appl. Phys.* **1994**, *75*, 3017.

oxynitrate as the zirconium source and report on the ferroelectric, dielectric, and optical properties of thin PbZrO_3 films grown on $\text{Pt/Ti/SiO}_2/\text{Si}$ substrates. The perovskite PbZrO_3 films of thickness 89–137 nm have good ferroelectric and dielectric properties. We use a classical dispersion formula to describe the dielectric function of thin PbZrO_3 films and assume a three-layer model (ambient/ PbZrO_3 /Pt) for PbZrO_3 on platinized silicon substrates. A good fit of the model to the measured Ψ and Δ data of spectroscopic ellipsometer has been obtained.

Experimental Section

Preparations of PbZrO_3 Thin Films by a Chemical Solution Deposition (CSD) Process. Lead acetate trihydrate ($\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$) and zirconium oxynitrate dihydrate ($\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$) are the starting materials, and 2-methoxyethanol ($\text{C}_3\text{H}_8\text{O}_2$) is a solvent. Lead acetate trihydrate and zirconium oxynitrate dihydrate are initially dissolved in 2-methoxyethanol, in a 1:10 molar ratio of lead (or zirconium) to 2-methoxyethanol and a 1:1 molar ratio of lead to zirconium, and then stirred for 30 min at 70 °C. The precursor with 10% excess Pb composition was prepared for the purpose to compensate for the lead loss in the deposition process. Without reflux and high-temperature distillation to remove water, the concentration of the final solution can be adjusted to 0.2–0.3 M by adding 2-methoxyethanol. The whole process of the preparation of the precursor solution is performed in an ambient atmosphere.

Before spin-coating on the substrates, the solution is filtered by the porous site of the filter paper to avoid particulate contamination. The thermal treating process for the samples is completed in a hot plate and a rapid thermal annealing (RTA) furnace. The coating solution of PbZrO_3 films was deposited onto $\text{Pt}(111)/\text{Ti}/\text{SiO}_2/\text{Si}(100)$ substrates by spin-coating at 3600 rpm for 30 s. After each spin-coating process the samples were heat-treated at 350 °C for 30 min in an air atmosphere by using a hot plate. This step is repeated several times to obtain the desired thickness of the films. The PbZrO_3 films on $\text{Pt/Ti/SiO}_2/\text{Si}$ substrates annealed at 650 °C for 5 min by RTA in an oxygen atmosphere. The heating rate was 100 °C/s. The thickness of the annealed films was measured by a spectroscopic ellipsometer (SE).

The crystalline structure of the PbZrO_3 films on $\text{Pt/Ti/SiO}_2/\text{Si}$ substrates were analyzed by a D/Max- γB (Ragaku, Japan) rotating X-ray diffractometer (XRD) with $\text{Cu K}\alpha$ radiation in the angle range from 18° to 60°. The surface morphologies and roughness of PbZrO_3 thin films were obtained by a NanoScope IIIA (Digital Instruments, Santa Barbara, CA) atomic force microscope (AFM). The grain sizes of the thin films were observed from the AFM images. To investigate the ferroelectric properties of thin PbZrO_3 films, the top electrodes of gold (Au) of diameter 0.2 mm were prepared on the top surface of the PbZrO_3 films through a shadow mask in a vacuum evaporation system. The polarization vs electric field (P – E) loop of the specimens was measured using a standard ferroelectric tester (RT66A, Radiant Technologies). The dielectric permittivity and capacitance (C)–voltage (V) characteristic of the specimen were measured by an HP 4194A impedance analyzer instrument with a small ac signal of 50 mV. The refractive index n and the extinction coefficient k of thin PbZrO_3 films were obtained by spectroscopic ellipsometry (SE). Ellipsometric measurements were carried out by a variable-angle spectroscopic ellipsometer (VASE, J.A. Wollam Co., Inc.) in the 345–1700 nm range at 5 nm intervals with autoretarder. The measurement was carried out at angle of incidence of 70°.

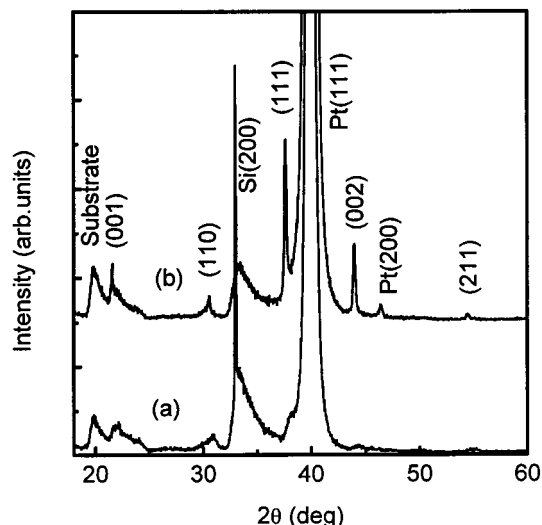


Figure 1. XRD pattern of PbZrO_3 thin films with various thicknesses grown on $\text{Pt/Ti/SiO}_2/\text{Si}$ substrates annealed at 650 °C for 5 min in an oxygen atmosphere by RTA: (a) 89 nm and (b) 137 nm.

Results and Discussion

Figure 1 shows the X-ray diffraction pattern of PbZrO_3 thin films with (a) 89 nm and (b) 137 nm grown on $\text{Pt}(111)/\text{Ti}/\text{SiO}_2/\text{Si}(100)$ substrates annealed at 650 °C for 5 min in an oxygen atmosphere by RTA. According to the XRD patterns in Figure 1, the PbZrO_3 film was polycrystalline structure. Several peaks of the PbZrO_3 film with thickness of 89 nm could be observed at 22.12°, 30.86°, 37.92°, 44.38°, and 54.94°. When the films thickness is 137 nm, these peaks shift at 21.58°, 30.56°, 37.62°, 43.98°, and 54.48°, which can be identified as the reflection from (001), (110), (111), (002), and (211), respectively. The peak at 21.58° corresponds to a lattice spacing of 0.411(4) nm. Assuming the crystalline structure of PbZrO_3 is a tetragonal perovskite unit, the lattice spacings of a and c can be defined as $a_T = 0.415(3)$ nm and $c_T = 0.411(4)$ nm, the results close to the reported values.¹⁶ The relative peak intensity of $I(111)/\Sigma I(hkl)$ was found to be 0.522, indicating remarkable (111) grain orientation.

Figure 2 shows the AFM images of PbZrO_3 thin films with (a) 89 nm and (b) 137 nm on $\text{Pt/Ti/SiO}_2/\text{Si}$ substrates annealed at 650 °C for 5 min in an oxygen atmosphere by RTA. On the surface image of films, many clusters are found which are composed by nano-size grains in size of about 150–200 nm. The root-mean-square (rms) roughness of the films with thicknesses 89 and 137 nm are 4.4 and 7.2 nm, respectively. The thicker the film, the larger the rms roughness. The grain is square, and the average grain size is about 180 nm for the samples with different thick annealed at 650 °C.

Figure 3 shows a typical polarization–electric field (P – E) hysteresis loop for the 89 nm thick PbZrO_3 film on $\text{Pt/Ti/SiO}_2/\text{Si}(100)$ substrate, annealed at 650 °C for 5 min in the oxygen atmosphere by a RTA process. The measurement was performed at an applied voltage of 5.5 V. The average remanent polarization (P_r) and the coercive electric field (E_c) obtained from the P – E hysteresis loops are 5.0 $\mu\text{C}/\text{cm}^2$ and 230 kV/cm, respec-

(15) (a) Zeng, J.; Song, S.; Wang, L.; Zhang, M.; Zhang, L.; Lin, C. *J. Am. Ceram. Soc.* **1999**, *82*, 461. (b) Meng, X. J.; Cheng, J. G.; Li, B.; Guo, S. L.; Ye, H. J.; Chu, J. H. *J. Cryst. Growth* **2000**, *208*, 541. (c) Shao, Q.; Li, A.; Ling, H.; Wu, D.; Wang, Y.; Ming, N. *Mater. Lett.* **2001**, *50*, 32.

(16) Kanno, I.; Hayashi, S.; Kitagawa, M.; Takayama, R.; Hirao, T. *Appl. Phys. Lett.* **1995**, *66*, 145.

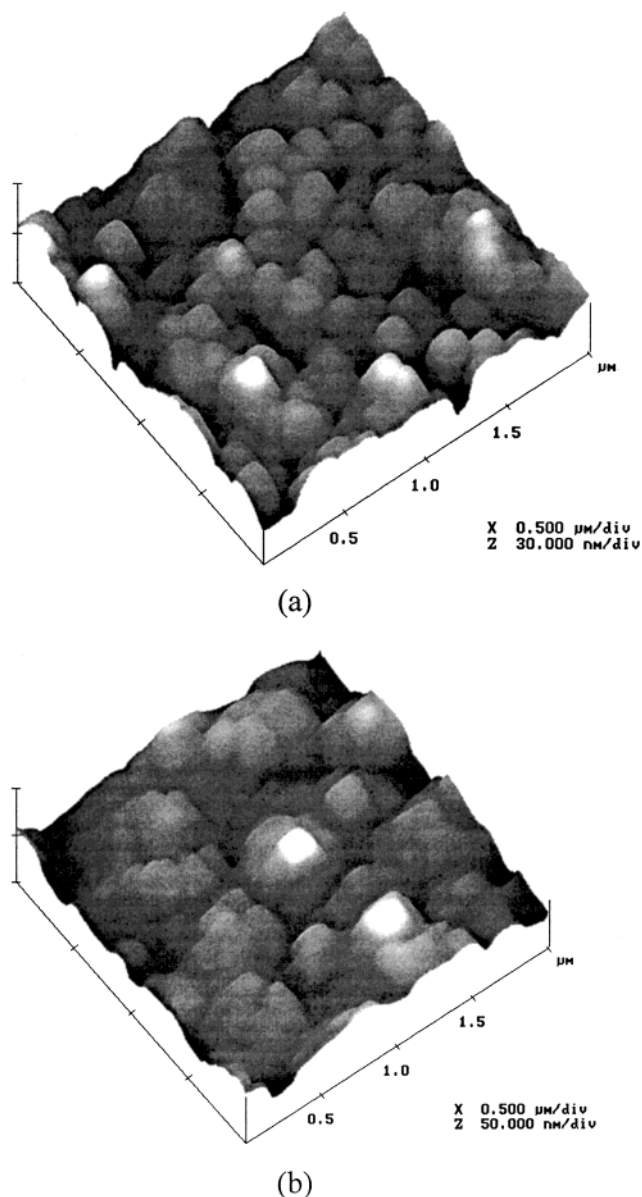


Figure 2. AFM images of PbZrO₃ thin films of Figure 1.

tively. For the 137 nm thick PbZrO₃ film, the average remanent polarization (P_r) and the coercive electric field (E_c) obtained from the P - E hysteresis loops are $7.4 \mu\text{C}/\text{cm}^2$ and $210 \text{ kV}/\text{cm}$, respectively, at applied voltage of 8 V. The spontaneous polarization is lower, and the coercive electric field is higher than that in similar PZT films,^{2,6} which is not good ferroelectrics. Kanno et al.¹⁶ have reported the same result, that 87.5 nm PbZrO₃ films are ferroelectric. Chattopadhyay et al.¹³ reported that PbZrO₃ films thinner than 300 nm are ferroelectric when they exhibit a hysteresis loop. Thus, the normally antiferroelectric PbZrO₃ appears to undergo a transition to a ferroelectric phase with decreasing thickness. It could arise simply from interfacial strain due to lattice mismatch. Such strain would be more important for thinner films.¹⁷ The origin of the film strain includes incomplete relaxation of lattice mismatch with the substrate by misfit dislocations, thermal expansion

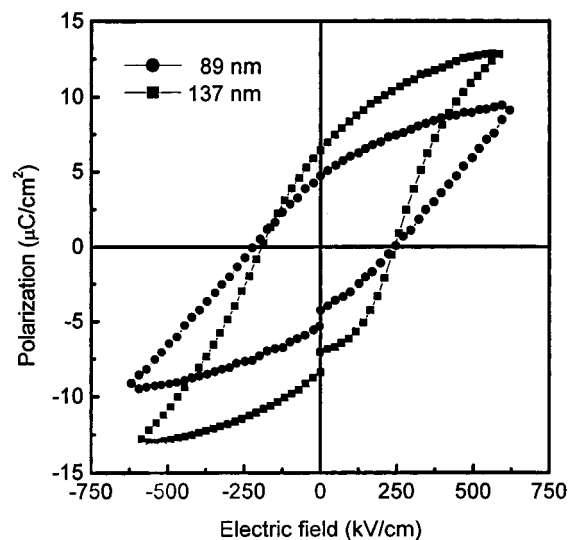


Figure 3. Typical P - E hysteresis loops for PbZrO₃ thin films of Figure 1.

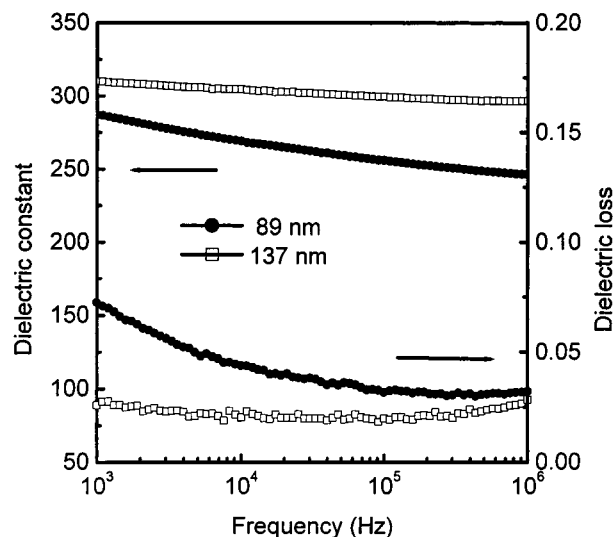


Figure 4. Dielectric constant and dissipation factor of the PbZrO₃ thin films of Figure 1 as a function of the frequency.

mismatch between the film and substrate, and most importantly strains associated with the paraelectric state to ferroelectric transformation.¹⁸

The dielectric constant and dissipation factor measurements were made at room temperature as a function of frequency in the range of 1 kHz–1 MHz for the films deposited on Pt/Ti/SiO₂/Si substrates. Figure 4 shows the variation of dielectric constant and dissipation factor with the frequency for the PbZrO₃ thin films of 89 and 137 nm deposited on Pt/Ti/SiO₂/Si substrates. The dielectric constant and dissipation factor decrease from 287 and 0.073 to 246 and 0.032 with increasing frequency from 1 kHz to 1 MHz, respectively, for 89 nm thick PbZrO₃ film. The dielectric constant and dissipation factor decrease from 310 and 0.026 to 297 and 0.028 with increasing frequency from 1 kHz to 1 MHz, respectively, for 137 nm thick PbZrO₃ films. At 100 kHz,

(17) (a) Pertsev, N. A.; Zembilgotov, A. G.; Waser, R. *J. Appl. Phys.* **1998**, *84*, 1524. (b) Pertsev, N. A.; Zembilgotov, A. G.; Tagantsev, A. K. *Phys. Rev. Lett.* **1998**, *80*, 1988.

(18) (a) Streiffer, S. K.; Parker, C. B.; Romanov, A. E.; Lefevre, M. J.; Zhao, L.; Speck, J. S.; Pompe, W.; Foster, C. M.; Bai, G. R. *J. Appl. Phys.* **1998**, *83*, 2742. (b) Romanov, A. E.; Lefevre, M. J.; Speck, J. S.; Pompe, W.; Streiffer, S. K.; Foster, C. M. *J. Appl. Phys.* **1998**, *83*, 2754.

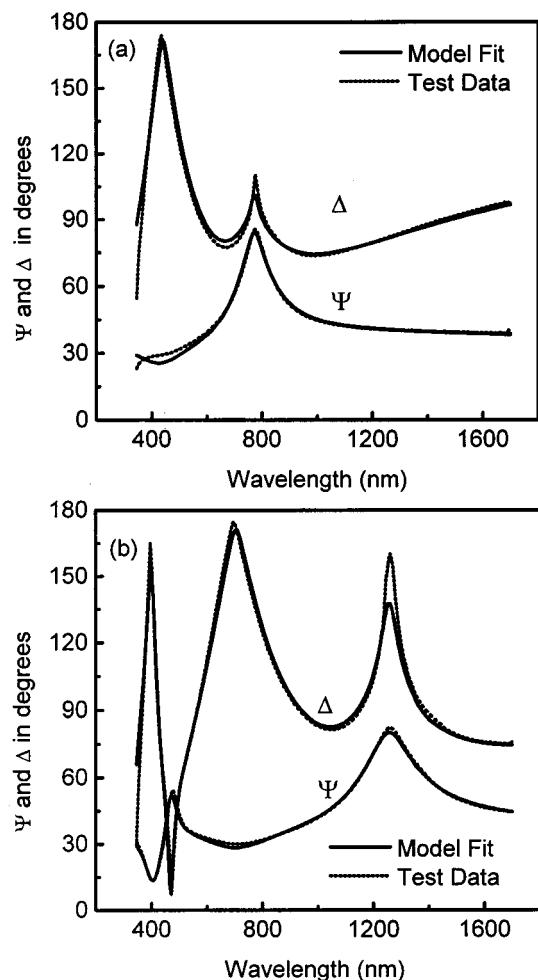


Figure 5. Spectra of the ellipometric parameter Ψ and Δ for PbZrO_3 thin films of Figure 1.

the dielectric constant and dissipation factor of 89 and 137 nm thick PbZrO_3 films are 256 and 0.032 and 300 and 0.020, respectively. The results comparable to those reported by Li et al. ($\epsilon_r = 200\text{--}250$, $\tan \delta = 0.02\text{--}0.03$)¹¹ and Kanno et al. ($\epsilon_r = 400$).¹⁶

Figure 5 shows the spectra of ellipometric parameter Ψ and Δ of PbZrO_3 thin films with thickness of 89 and 137 nm as functions of wavelength. In the lower energy range, the spectra exhibit oscillations due to the interference between multiple reflected beams within the film, which correspond to the "transparent" range of the film. This transparent region is identical with that of the transmission spectrum shown in Figure 5. The oscillating frequency depends on the thickness of the thin film. Generally, the thicker the films, the lower the frequency.

We used as "three-layer model" composed (ambient/ PbZrO_3 /Pt) to analyze the ellipsometric spectra. The reflective index n and extinction coefficient k as functions of wavelength, as well as the thickness of the film, are determined by an optimization process. Two- and three-layer PbZrO_3 thin films are coated on Pt/Ti/SiO₂/Si substrates by CSD processing; the thickness of the films is 89 and 137 nm, respectively. The refractive index and the thickness of these thin films grown on Pt-coated Si substrates were measured by VASE. The experimental data were fitted using a Cauchy dispersion

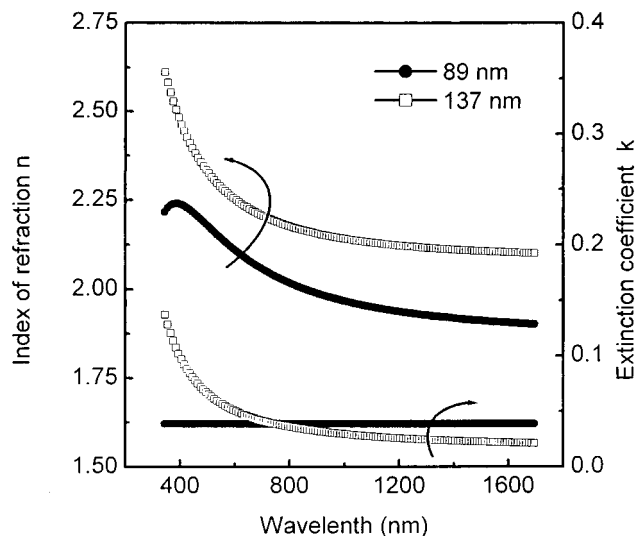


Figure 6. Wavelength dependence of the refractive index n and the extinction coefficient k of PbZrO_3 thin films of Figure 1.

relationship and the Urbach absorption model,¹⁹

$$n = A_n + \frac{B_n}{\lambda^2} + \frac{C_n}{\lambda^4} \quad (1)$$

$$k = A_k \exp \left[B_k \left(1.24 \left(\frac{1}{\lambda} - \frac{1}{C_k} \right) \right) \right] \quad (2)$$

where A_n , B_n , C_n , A_k , and B_k are constants, $C_k = 400$ nm is the absorption limit, and λ is the wavelength of light in micrometers. For the PbZrO_3 film with a thickness of 89 nm, A_n , B_n , C_n , A_k , and B_k are 1.864, 0.1123, -8.359×10^{-3} , 3.890×10^{-2} , and 0, respectively. For the PbZrO_3 film with a thickness of 137 nm, A_n , B_n , C_n , A_k , and B_k are 2.793, 6.166×10^{-2} , -1.979×10^{-4} , 9.918×10^{-2} , and 0.6528, respectively. The refractive indexes n and extinction coefficient k spectra of PbZrO_3 films with thickness of 89 and 137 nm on Pt-coated Si substrates are shown in Figure 6. The refractive index n of crystalline PbZrO_3 film with a thickness of 89 nm increases from 2.238 to 2.240 and then decreases to 1.90 in the wavelength range 345–1700 nm. The refractive index n of crystalline PbZrO_3 film with thickness of 137 nm decrease from 2.644 to 2.101 with increasing wavelength range 345 to 1700 nm. At 633 nm, the refractive indexes n are 2.093 and 2.236 for the films with thickness of 89 and 137 nm, respectively. The refractive index of 137 nm thick PbZrO_3 film is larger than that of 89 nm thick thin film. The value of the 137 nm thick film is a little larger than that of MOD PbZrO_3 films (2.125).²⁰ The 137 nm thick PbZrO_3 thin films have a large refractive index, high dielectric constant, and low dissipation factor; a possible reason might be the internal stress of the films originated from the film growth as well as the high quality of the film.¹⁶ The extinction coefficient k is a constant for the 89 nm thick thin film, implying that the 89 nm thick PbZrO_3 film is transparent; for the 139 nm thick PbZrO_3 film,

(19) (a) Barradas, N. P.; Keddle, J. L.; Sackin, R. *Phys. Rev. E* **1999**, 59, 6138. (b) Yu, G.; Soga, T.; Shao, C. L.; Jimbo, T.; Umeno, M. *Appl. Surf. Sci.* **1997**, 113/114, 489.

(20) Zametin, V. I. *Phys. Status Solidi B* **1984**, 124, 625.

the extinction coefficient k is smaller than 0.15 in the wavelength range from 345 to 1700 nm.

Conclusions

In conclusion, well-crystallized PbZrO_3 thin films were grown on $\text{Pt/Ti/SiO}_2/\text{Si}(100)$ substrate by a chemical solution deposition route and spin-coating processing. XRD, AFM, spectroscopic ellipsometry, and electrical measurements were used to determine the characteristics of PbZrO_3 thin films. The square grain size is about 180 nm exhibited in the PbZrO_3 film. The 137 nm thick PbZrO_3 film exhibited remanent polarization and the coercive electric field value of $7.4 \mu\text{C}/\text{cm}^2$ and 210 kV/cm, respectively, at an applied value of 8

V. At 100 kHz, the dielectric constant and dissipation factor of 89 and 137 nm thick PbZrO_3 films are 256 and 0.032 and 300 and 0.020, respectively. At 633 nm, the refractive index n and extinction coefficient k of 137 nm thick PbZrO_3 thin film are 2.236 and 0.0474, respectively.

Acknowledgment. This work is supported by the Centre for Smart Materials of the Hong Kong Polytechnic University, the K.C. Wong Education Foundation of Hong Kong, and the National Natural Science Foundation of China (No. 59995520).

CM010392O