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The effect of dual complexing agents of lactic and citric acids on the formation of sol-gel derived Ag–$PbTiO_3$ percolative thin film

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ABSTRACT

Controlling the formation of conductive particles to be nano-scale is important for achieving percolation effect in metal dispersed thin film composite to contribute extraordinary dielectric properties required for miniaturization of electronic devices. In this paper, lactic acid (LA) and citric acid (CA) were used as dual complexing agents to prepare a typical Ag nanoparticle dispersed $PbTiO_3$ (PTO) composite thin film by using a sol-gel method. The phase structure of the thin film and the coordination effect between complexing agent and metallic ions were investigated. It revealed that LA coordinated with Ti^{4+} and Pb^{2+} and CA coordinated with Ag^{+}. Lead was fixed inside the gel network by LA and restricted to evaporate during heat treatment thus the pyrochlore phase was prevented from forming in the thin film. Ag^{+} was coordinated by CA and the diffusion and thus aggregation of silver during gelation and annealing process were weakened. Silver nanoparticles dispersed in the PTO matrix formed with dual complexing agents of LA and CA introduced during the preparation process. The composite thin film of perfect perovskite phase with silver nanoparticles embedded was obtained at the molar ratio of LA/lead = 0.5 and CA/lead = 0.5. The dielectric constant of the thin film with silver nanoparticles is 5 times higher than that without silver nanoparticles.

1. Introduction

The perovskite phase based materials have attracted much attention due to their excellent dielectric properties, such as the high dielectric constant, which are important for applications of capacitors and high-storage devices [1–4]. Percolative composite materials by introducing metallic phase particles into the perovskite phase matrix are proved to be excellent materials with high dielectric properties [5–7]. According to the percolation theory [8], the metal-dielectric composite material in which metallic phase is dispersed as small particles uniformly in the system will undergo a nonlinear transition from insulator to conductor with the increase in concentration of metallic phase to be a specific value named percolation threshold, where metallic particles begin to make contact with each other to form a conducting path. Meanwhile, when the concentration of the metallic phase is approaching the percolation threshold, the dielectric constant would be also enhanced by several orders of magnitude compared with the traditional perovskite materials [9–11]. Moreover, thin films are being developed significantly in recent years in the miniaturization of electronic devices. Improving the dielectric properties of the thin films would be therefore the most important thing of electronic technology [12–15]. However, it is hard to obtain the percolation effect in thin film with metallic phase dispersed uniformly since the thickness of thin film is only hundreds of nanometers in usual. Metallic particles inside the thin films would be easy to connect with each other to form conductive paths if the size of the metallic phase particles was nearly the same as the thickness of thin films. It will make the percolation effect disappear and the dielectric thin films even become conductive [16]. Therefore, the size of metallic particles is required to be strictly within nano-scale for the metallic phase dispersed thin film composites with percolation effect and high dielectric properties [17].

In general, the metallic particles have strong potentials to aggregate to form large sized particles and are difficult to be controlled as nano-scaled ones in the percolative $PbTiO_3$ (PTO) thin film [18,19]. But in the recent year [10], silver nanoparticles (Ag) are prepared in Ag–PTO composite thin films through a lead-excess (Pb) system in which Ag–Pb alloy particles form initially as a transitional phase and then decompose into nano-scaled Ag. Nevertheless, the preparation route might be not so appropriate for atmosphere protection since the excessive lead exists in the system which will evaporate during the transition of Ag–Pb alloy into silver nanoparticles although it is an important way to prepare the nano-silver particle dispersed percolative PTO thin film. Therefore it is significantly important to find an effective way to prepare the percolative thin film without introducing excess lead into the system. It would be much better for air protection and a progressive way to prepare silver nanoparticles in the percolative thin film.

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Herein, the PTO thin film prepared by a common sol-gel method with the addition of silver as metallic phase is proposed. Other than stoichiometric PTO without excess lead, the dual complexing agents are used in which one is to pin lead ion into network to form a dense matrix and the other is to bind Ag ions for restraining the diffusion and aggregation of Ag in the thin film. Therefore it would be most probably an important method to control silver to be nano-sized particles in PTO without excess lead. It is worth noting that the PTO is a typical perovskite phase and Ag is a typical metallic conductive phase. In this work, the formation process of metallic particles and perovskite phase was investigated. The well crystallized PTO thin film with silver nanoparticles dispersed uniformly was obtained, in which the silver nanoparticles are formed in situ without introducing excess lead into the system and by only a one step process, which are quite progressively different from that shown in a previous work.

2. Experimental details

The Ag–$PbTiO_3$ composite thin films were prepared by a sol-gel route using lead nitrate ($Pb(NO_3)_2$), tetrabutyl titanate ($Ti(C_4H_9O)_4$) and silver nitrate ($AgNO_3$) as starting materials. Initially 1 mol of tetrabutyl titanate was dissolved in 1 l of ethylene glycol monomethyl ether ($HOCH_2CH_2OCH_3$) and then it was stirred at room temperature for about 20 min to obtain the mixed solution. After that the nitric acid (HNO_3) was added into the mixed solution in which the molar ratio of HNO_3/Ti was controlled to be 1:1. The clear and stabilized solution of Ti was finally obtained. Secondly, 1 mol of lead nitrate, which was atomic–stoichiometric with titanium, was dissolved into the 1 l of solvent in which water and ethylene glycol monomethyl ether with a volume fraction of 1:9 (v/v) was controlled and then it was stirred at temperature between 70 and 80 °C for about 20 min to obtain the lead solution. Meanwhile, different contents of lactic acid (LA) or citric acid (CA) were added into lead solution as complexing agents. The molar ratios of LA/Pb were controlled to be 0, 0.5 and 1 and that of CA/Pb was controlled to be 0, 0.5, 1, 3 and 5 (c/c). After that the as prepared Pb solution and Ti solution were mixed with a stoichiometric ratio of 1:1 (c/c) to obtain the Pb–Ti solution. Finally, the silver nitrate and ethylene glycol monomethyl ether were added into the Pb–Ti stoichiometric solution to form the precursor solution, in which the molar ratio of Ag/Ti was controlled to be 0.1 and ethylene glycol monomethyl ether was as solvent to modify concentration of the precursor solutions to be 0.2 mol/l.

The wet layers were prepared using the as prepared precursor solutions by dip coating method with the withdraw speed of 4 cm/min on cleaned indium tin oxide/glass substrates and dried under an infrared lamp. After that they were heat treated in a muffle furnace at 600 °C for 10 min to be calcined and cooled down to room temperature naturally in air. And then, dip coating and heat treatment processes were repeated to obtain multiple processed Ag–$PbTiO_3$ thin films with a thickness of about 300 nm (±16 nm). Finally, the thin films were annealed again in air at 600 °C for 3 h.

The crystalline phase structure of the thin films was characterized by an X-ray diffractometer (Rigaku D/max-rA at 36 kV and 30 mA) with a Cu K_α radiation of 0.15418 nm, sampling interval of 0.02° and scanning speed of 4 degrees per minute. The morphology of the samples was observed in secondary electron imaging mode by scanning electron microscopy (SEM, HitachiSEM-S-570) with an operating voltage of 5 kV and transmission electron microscopy (TEM, Philips CM200UT). The coordination between metal ions and complexing agents of LA and CA was characterized by Fourier transform infrared spectra (FT-IR, Nicolet-Avatar360). The formation and particle size of silver nanoparticles were detected by absorption spectra of ultraviolet–visible (UV–VIS) light using a spectrophotometer (Perkin-Elmer-Lamba-20). The dielectric properties were measured by an LCZ meter (Keithley3330).

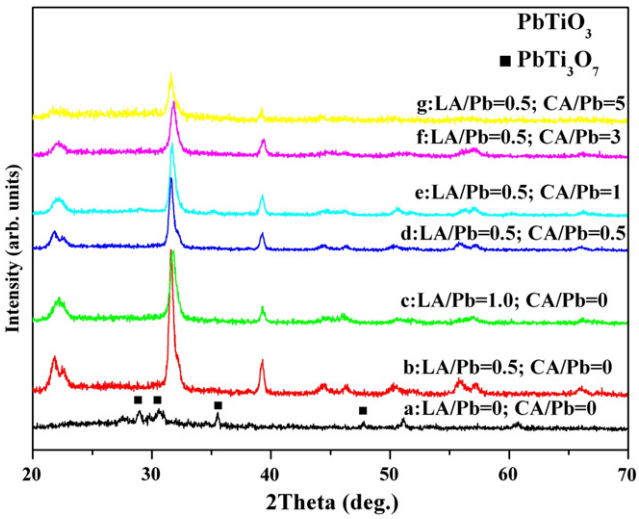

Fig. 1. XRD patterns of the thin films prepared with different contents of LA and CA as complexing agent.

3. Results

Fig. 1 shows X-ray diffraction (XRD) patterns of the thin films prepared with different contents of LA and CA added as complexing agents. It can be seen that the thin film without the addition of LA shows mainly the pyrochlore phase with little perovskite phase. In contrast, the thin films prepared with the addition of LA exhibit the perfect perovskite phase without the pyrochlore, while the content of the perovskite phase decreases with increasing molar ratio of LA/Pb from 0.5 to 1.0 (c/c). In addition, when the molar ratio of LA/Pb is fixed to be 0.5, the perovskite phase content decreases with increasing the content of CA.

Fig. 2 shows the infrared spectra of sol solutions with different compositions. The absorption peaks at 3419 cm^{-1} and 1388 cm^{-1} appearing in all systems have been proved to be hydrogen bond among water molecules [20] and N – O vibration in NO_3^- [21], respectively. The absorption band around 800–1000 cm^{-1} appearing in all systems except one without Ti ions has been proved to be Ti – O – C vibration [22]. The peaks around 1051 cm^{-1} and 1735 cm^{-1} appear in the systems with LA and a light blue shift from 1051 to 1056 cm^{-1} and from 1735 to 1767 cm^{-1} appears for systems with adding Ti in LA

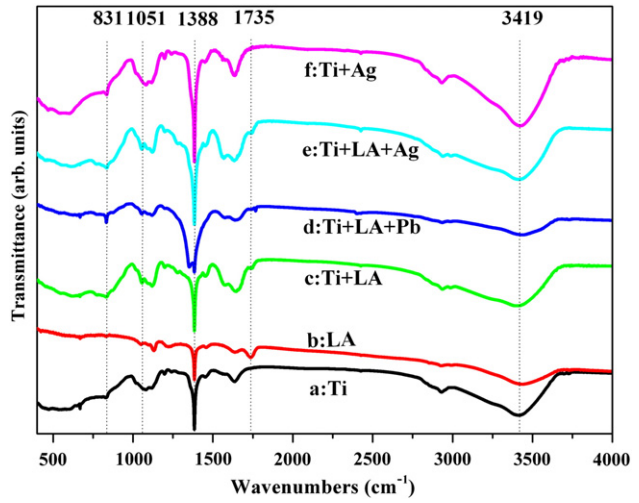

Fig. 2. FTIR spectra of solutions derived from different components dissolved in ethylene glycol monomethyl ether and water with nitric acid as stabilizer, where Ti is tetrabutyl titanate, Pb is lead titanate and Ag is silver nitrate.