Enhancement of Polarization in Ferroelectric Films via the Incorporation of Gold Nanoparticles

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ABSTRACT: Ferroelectric thin films have been extremely studied for many applications such as nonvolatile memories, super capacitors, and solar cells. For these devices, improving the polarization properties of ferroelectric thin films is of great significance to their performance. Here, Au–lead zirconate titanate (PZT) nanocomposite thin films were prepared by a simple one-step chemical solution deposition (CSD) method on silicon substrates, and the effects of Au concentration on the ferroelectric properties were investigated. The experimental results show that the remanent polarization of the Au–PZT films with 1.2 mol % Au is about 80 μC/cm², which is 50% higher than that of the pure PZT thin films. On the basis of the analysis of chemical valences, the enhanced polarization properties can be ascribed to the interaction between Au nanoparticles (Au NPs) and PZT at the Au–PZT interfaces. Our results demonstrate that the incorporation of an appropriate amount of Au NPs is an effective way to enhance the polarization properties of ferroelectric films. The Au–PZT nanocomposite thin films with excellent polarization properties on silicon substrates are expected to be widely used in integrated ferroelectric devices.

1. INTRODUCTION

Ferroelectric thin films, such as Pb(ZrTi)O₃, Pb(VDF-TrFE), and BiFeO₃, have attracted much attention owing to their unique dielectric, optical, and conductive properties, 1–3 which are not very meaningful for the polarization-controllable functional thin-film devices. In addition, the action mechanism of metal NPs and ferroelectric thin films without defects could be prepared. 4 In addition, the remnant polarization could be markedly enhanced under biaxial compressive imposed by coherent epitaxy in strained BaTiO₃ thin films. 5 By using suitable single-crystal substrates and growth parameters, the epitaxial ferroelectric thin films without defects could be prepared. 4 In addition, the remnant polarization could be markedly enhanced under biaxial compressive imposed by coherent epitaxy in strained BaTiO₃ thin films. 5 However, in these studies, nonsilicon-based single-crystal substrates and complicated techniques are required, restricting the commercial applications.

On the other hand, to improve the electrical properties of ferroelectric thin films, noble metal nanoparticles (NPs) owning unique dielectric, optical, and conductive properties have been composited with ferroelectric films. 6–12 Yang et al. successfully incorporated Au NPs into BaTiO₃ thin films and found that the Au–BaTiO₃ nanocomposite films exhibited unique surface plasma resonance and superfast nonlinear optical response. 16 Paik et al. have investigated the effect of Ag NPs on the remanent polarization of the Ag–P(VDF-TrFE) composite films and found that the remanent polarization value increased to 10–12 μC/cm² with respect to P(VDF-TrFE) films (7–8 μC/cm²). 17 The Pt–lead zirconate titanate (PZT) composite powders could be synthesized by the conventional solid-state reaction and showed an improved dielectric tunability by 460% and ferroelectric properties by 13%. 19 Although the remanent polarization could be increased in metal NPs/ferroelectric nanocomposite, the values were still too small as compared with ferroelectric epitaxial thin films. Furthermore, most of the previous studies on metal NPs/ferroelectric composites have just focused on the composite powders and dielectric and optical properties, 13,16 which are not very meaningful for the polarization-controllable functional thin-film devices. In addition, the action mechanism of metal NPs remains unclear. 14,17,20 For instance, Tsutsu et al. attributed the enhanced polarization to the interfacial polarization at the...
interface of NPs/ferroelectric films.\textsuperscript{14} Cheng et al. thought that the electric field could be locally intensified near the embedded Pt NPs to promote domain nucleation.\textsuperscript{20} The enhancement of effective field and the compensation of local polarization mismatch have also been reported to explain the increased ferroelectric properties in metal NPs/ferroelectric composite films.\textsuperscript{20} Therefore, it is still a key problem to understand the enhancement mechanism of polarization properties in metal NPs/ferroelectric nanocomposite films.

In this study, we attempted to use Au NPs to prepare Au–PZT nanocomposite thin films by a simple one-step chemical solution deposition (CSD) method on silicon substrates and systematically study the effect of the amount of Au NPs on ferroelectric properties. The experimental results show that the remnant polarization of Au–PZT nanocomposite films can reach \(80 \mu \text{C/cm}^2\), which is almost the same as that of some high-quality epitaxial PZT thin films. On the basis of the analysis of chemical valences of elements in the nanocomposite films, the enhancement in electric properties can be ascribed to the charge transfer at the PZT–Au interfaces. Our results not only demonstrate that the ferroelectric films can present remarkable ferroelectric properties with an appropriate amount of Au NPs, but also reveal the mechanism of the effect of Au NPs on ferroelectricity.

2. RESULTS AND DISCUSSION

In our previous work, we found that the crystallization temperature of PZT was above 500 °C\textsuperscript{21,22} and HAuCl\textsubscript{4} decomposed easily to form Au NPs at a heating temperature over 200 °C.\textsuperscript{23} Accordingly, in the annealing process, the Au NPs will form before the crystallization of amorphous PZT matrix for the Au–PZT composite films. Figure 1 shows an ideal schematic of the Au–PZT nanocomposite film in which the Au NPs are uniformly distributed in the PZT matrix.

![Figure 1. Schematic diagram for the Au–PZT nanocomposite film and testing electric properties.](image)

To determine the existing form of Au in the composite films, the chemical valence of Au in the composite films was investigated by X-ray photoelectron spectroscopy (XPS). Figure 2 shows the XPS spectra of Au 4f for the Au–PZT composite films with different Au concentrations. Compared with the pure PZT film (Figure 2a), Au 4f core-level spectrum can be detected in the composite films (Figure 2b–d). One peak with a higher binding energy (87.7 eV) is identified as Au 4f\textsubscript{3/2} core-level line, and another one with a lower binding energy (84.0 eV) is identified as Au 4f\textsubscript{1/2} core-level line, which are consistent with the values reported for pure metal Au.\textsuperscript{23,24} This result indicates that Au exists in the composite films as the elementary substance rather than the compound.

Figure 3 shows X-ray diffraction (XRD) patterns of the Au–PZT composite films with different Au concentrations. As shown in Figure 3a, the pure PZT films are crystallized into the perovskite phase without any secondary phase. In the Au–PZT composite films with 0.6 mol % Au, in addition to the diffraction peaks of the perovskite phase of PZT, two relatively weak diffraction peaks can be observed (Figure 3b), which correspond to the diffraction peaks of (111) and (200) planes of the face-centered cubic structure of Au, respectively. The diffraction peaks of Au(111) and Au(200) become more pronounced with the increasing Au concentration (Figure 3c–f). The results indicate that there are two phases of the perovskite PZT and the face-centered cubic structure of Au in the Au–PZT composite films. This is in full agreement with the XPS results. As mentioned previously, the XPS results reveal that elementary gold exists in the composite films. It can also be seen from Figure 3 that compared with the pure PZT film, the location of the diffraction peaks of the PZT perovskite phase in the composite films has not changed. The result gives two important pieces of information: (1) the Au atoms did not dissolve into the PZT perovskite phase, namely, the addition of Au has no doping effect on the perovskite phase of PZT and (2) the presence of Au particles did not change the stress state of the films. Therefore, the effects of stress and doping on the ferroelectric properties of the composite films can be ruled out according to the above results.

Figure 4 shows the cross-sectional images of the pure PZT film and the Au–PZT composite films with the Au concentrations of 1.2 and 12 mol %. The pure PZT film shows a columnar grain structure (Figure 4a). In the Au–PZT composite film with 1.2 mol % Au, the columnar grain structure can also be observed, but in which uniformly dispersed Au NPs with an average size of about 5 nm appear (Figure 4b). As shown in Figure 4c, when the Au concentration increased to 12 mol %, the columnar grain structure of the perovskite PZT disappeared, and Au NPs are aggregated into larger Au particles and distributed unevenly. Namely, the size of Au NPs increases with the increasing amount of the Au concentration. Even more serious is the emergence of microcavity in the composite films with higher Au concentrations. Figure 5 shows a high-resolution transmission electron microscopy (HRTEM) image for the Au nanoparticle (Au NPs) in the Au–PZT nanocomposite films. It can be inferred that the electric properties of the composite films have a higher concentration of Au than 12 mol %, a large number of relatively large Au particles can hinder the growth of columnar PZT grains. Accordingly, the columnar grain structure disappears. Thus, in annealing process, Au NPs were formed before the crystallization of amorphous PZT matrix and may affect the growth of the perovskite phase of PZT in the crystallization process. In the Au–PZT composite film with a higher concentration of Au than 12 mol %, a large number of relatively large Au particles can hinder the growth of columnar PZT grains. Accordingly, the columnar grain structure disappears because of the disorder growth of the PZT grains, even leading to the formation of microcavities. According to the characteristics of microstructures, it can be inferred that the electric properties of
the Au−PZT films may become poor with adding a high Au concentration.

Figure 6 shows P−V hysteresis loops of the Au−PZT nanocomposite films with different Au concentrations measured at 1 kHz and 10 V. All of the films present symmetric P−V hysteresis loops. In addition, the P−V hysteresis loops are saturated at higher voltages, meaning that there is almost no
extrinsic contribution caused by the leakage current to polarization measurement. The remanent polarization of the composite films with 1.2 mol % Au concentration can reach above 80 μC/cm², which increased by almost 50% with respect to the pure PZT thin films. The enhancement in the remanent polarization is quite considerable, which can even be compared with some epitaxial PZT thin films. For comparison, the effects of Au concentration on the coercive voltage ($V_c$), remanent polarization ($P_r$), and saturation polarization ($P_s$) are summarized in Figure 7. It can be seen that with the increasing Au concentration from 0 to 1.2 mol %, coercive voltage ($V_c$) drastically decreases, whereas $P_r$ and $P_s$ remarkably increase. However, with further increase in Au concentration from 1.2 to 12 mol %, $V_c$ slightly decreases, whereas $P_r$ and $P_s$ substantially decrease. Obviously, the optimal Au concentration in the Au–PZT composite films is about 1.2 mol % where the best ferroelectric properties are realized. Also, the outstanding dielectric properties can be also achieved by adding Au NPs (Figure S1).

Usually, there are many factors, such as microstructure, stress, and element doping, that can affect the ferroelectric properties of ferroelectric films. First of all, the effect of microstructure on the ferroelectric properties is relatively large. In the Au–PZT composite films, when the Au concentration reaches 1.2 mol %, the columnar grain structure of the perovskite PZT begins to disappear and the Au NPs aggregate into the larger particles (Figure 4c). The density of the films also decreases because of the emergence of microvaccum (Figure 5). Therefore, the ferroelectric properties in the Au–PZT composite films with the Au concentration of 1.2 mol % become poor. By contrast, the Au–PZT composite films with the Au concentration of 1.2 mol % are very dense with no defect owing to the fact that Au NPs uniformly dispersed in the columnar grains of perovskite PZT (Figure 4b). Besides, the XPS and XRD results (Figures 2 and 3) proved that Au atoms did not enter the PZT lattice, and there was no change in the stress state of the composite films, thus the stress and doping effects can be excluded. To explain the increased ferroelectric properties in metal NPs/ferroelectric composite films, many hypotheses, such as the compensation of local polarization mismatch and enhancement of effective field, have been reported.

Unfortunately, they are not suitable for Au–PZT composite films or the Au–PZT composite films may be generated by the interaction between Au NPs and PZT matrix at the Au–PZT interface.

It has been accepted that the origin of ferroelectricity can be explained by the delicate balance between long-range Coulomb interactions favoring the ferroelectric phase and short-range forces favoring the paraelectric phase. Cohen and Krakauer et al. have demonstrated that the hybridization among lead 6s (Pb 6s), titanium 3d (Ti 3d), and oxygen 2p (O 2p) states is essential to weaken the short-range forces for PZT films by using the first-principles calculations. Therefore, ferroelectricity is strongly sensitive to Pb 6s, Ti 3d, and O 2p hybridization, which means the chemical valences of Pb, Ti, and O could indirectly reflect the ferroelectricity. Recently, the investigation of chemical valences of elements for ferroelectric perovskite oxides has been widely studied by XPS. Figure 8 shows the XPS results of O 1s, Ti 2p3/2, Zr 3d3/2, and Pb 4f7/2 for the Au–PZT nanocomposite films with increase in the concentration of Au.

Figure 7. (a) Coercive voltage, (b) remanent polarization, and (c) saturation polarization of the Au–PZT nanocomposite films as a function of the concentration of Au.

Figure 8. Changes of binding energies of O 1s, Ti 2p, Zr 3d, and Pb 4f for the Au–PZT nanocomposite films with different Au concentrations. The binding energy of O 1s is no significantly different and Zr 3d7/2 and Pb 4f7/2 only vary slightly in these Au–PZT films.
Figure 9 is a schematic diagram showing the mechanism for the charge transfer at the PZT–Au interface and energy band diagram of the Au–PZT nanocomposite films.

Figure 9. Schematics of the mechanism of charge transfer at the PZT–Au interface and energy band diagram of the Au–PZT nanocomposite films.

diagram of PZT in the Au–PZT films. First, the O 2p state makes bonds with Pb 6s state by a $\sigma_{\text{PbO}}$ state and the antibonding state of $\sigma^*_{\text{PbO}}$ state, and then these $\sigma_{\text{PbO}}$ and $\sigma^*_{\text{PbO}}$ states make bonds with the Ti 3d state by $\sigma_{\text{PbO}}$–$\pi$, $\sigma^*_{\text{PbO}}$–$\pi$, $\sigma^*_{\text{PbO}}$–$\pi^*$, and $\sigma^*_{\text{PbO}}$–$\pi^*$ states. On the basis of the discussion by Miura and Vanderbilt et al.,$^{33-35}$ the occupancy of electrons in both $\pi$ states and no electrons in $\pi^*$ make the $\pi$ bonds between the O 2p state and Ti 3d state the strongest, which corresponds to the perfect PZT. If another electron enters the unit cell of PZT or one electron escapes from the unit cell of PZT, the $\pi$ bond will be weakened leading to weakened ferroelectricity. For the actual preparation of PZT films, the volatilization of lead is unavoidable and a few holes will appear forming p-type PZT films as the dotted arrow shown in Figure 9. Therefore, the ferroelectricity cannot achieve the ideal value. However, the absent electrons could be supplied by Au NPs in the Au–PZT films. Considering the addition of Au, the charge transfer is inevitable because of the different work functions between PZT film and Au NP. The working functions for typical p-type PZT and metal Au are about 5.8 and 5.1 eV, respectively.$^{31}$ At PZT–Au interfaces, owing to the prerequisite of energy continuity, the direction of charge transfer must be from Au NPs to PZT matrix to unify the Fermi level.$^{36}$ For perovskite ATiO$_3$ (A: Pb, Ba, etc.) ferroelectric oxides, the bottom of the conduction band is composed of Ti 3d orbitals, whereas the top of the valence band consists of O 2p orbitals. Therefore, the charge transfer takes place from Au 6s to Ti 3d at the PZT–Au interface, and some electrons participate in the hybridization by the $\sigma_{\text{PbO}}$–$\pi$ state as shown by the yellow arrow in Figure 9. As a result, the bonding states are full, and the antibonding states are empty, which is the same as the ideal unit cell of PZT. Hence, the change of orbital hybridization leads to the improvement of ferroelectricity. It should be noted that exceeding electron doping will also deteriorate ferroelectricity owing to the occupancy of $\pi^*$ state.$^{37,38}$ Thus, in addition to the microstructure, this may be another reason for the reduction of ferroelectric properties in the Au–PZT composite films with relatively high Au concentrations. In this study, the Au concentration in the Au–PZT composite films is about 1.2 mol % where the best ferroelectric properties are realized. There is no doubt that the ferroelectric properties can be further improved by optimizing the Au concentration and preparation conditions. On the basis of our results, it is believed that the Au–PZT nanocomposite thin films with superior electric properties on silicon substrates will be widely used in the integrated ferroelectric devices.

3. CONCLUSIONS

In this study, the Au–PZT nanocomposite thin films were prepared by the one-step CSD method on silicon substrates. In the composite films with the Au concentration of about 1.2 mol %, the Au NPs are uniformly distributed in PZT matrix. The composite films show an enhanced remanent polarization of above 80 $\mu$C/cm$^2$, which is 50% higher than that of pure PZT films. On the basis of the analysis of chemical valences of elements in the composite films, the enhancements in the electric properties can be ascribed to the charge transfer at the PZT–Au interface. The results demonstrate that adding an appropriate amount of Au NPs is a valid method to improve the polarization properties of ferroelectric thin films.

4. EXPERIMENTAL DETAILS

Au–Pb(Zr$_{0.4}$Ti$_{0.6}$)O$_3$ (Au–PZT) nanocomposite thin films with a thickness of 200 nm were grown on Pt/Ti/SiO$_2$/Si substrates by CSD. High-purity lead acetate (Pb(CH$_3$COO)$_2$), zirconium-n-propoxide ([Zr(OCH$_2$CH$_2$CH$_3$)$_4$]), titanium tetraisopropoxide (Ti((CH$_3$)$_2$CHO)), 2-propanol ((CH$_3$)$_2$CHOH), and gold chloride acid (HAuCl$_4$) were used to prepare the Au–PZT precursor solution. First, considering the volatility of lead, excess 10% lead was added into the PZT precursor solution to ensure the ideal atomic ratio of Pb/Zr/Ti = 1.0:0.4:0.6 as our previous works reported.$^{21,22}$ Then, on the basis of the molar ratio of 0.006–0.14:1 (Au vs PZT), HAuCl$_4$ was dissolved by 2-propanol solution to form HAuCl$_4$ solutions with 0, 0.0024, 0.00, 0.011, 0.021, and 0.055 mol/L. Finally, the PZT precursor solution and the different HAuCl$_4$ solutions were fully mixed together with a volume ratio of 1:1 to form Au–PZT precursor solutions. After the above steps, the Au–PZT precursor solutions were successfully prepared with the addition of 0, 0.6, 1.2, 2.5, 5, and 12 mol % Au, respectively. After aging for 24 h, the Au–PZT precursor solutions were spin-coated on the Pt/Ti/SiO$_2$/Si substrates, operated at 3000 rpm for 40 s. The coated films were dried at 120 °C for 10 min and then pyrolyzed at 350 °C for 10 min. To obtain the PZT thin films with the designed thickness, the steps mentioned above were repeated three times before annealing. Finally, the Au–PZT films were annealed in an electric furnace at 600 °C for 30 min.

The crystal structure and orientation of the Au–PZT composite films were analyzed by θ–2θ scan of XRD (Rigaku RINT2000, Cu Kα radiation). The microstructures of the composite films were characterized by TEM (Tecnai G2 F20). The TEM specimen were prepared by the standard procedure of cutting, gluing, slicing, grinding, and finally ion milling with Ar ions until they were electron transparent by using a Gatan precision ion-polishing system (PIPS 691; Gatan). The chemical valence of the ions in the Au–PZT composite films was determined by XPS (Therma ESCALAB 250; Al Kα source, 1486.60 eV, resolution: 400 meV, energy step: 0.1 eV). As shown in Figure 1, the top electrodes of Pt with an area of 0.2 mm$^2$ were deposited by sputtering on the surface of the Au–PZT thin films to form a Pt/Au–PZT/Pt capacitor structure for testing electric properties. The ferroelectric properties of the composite films were measured by using a standard ferroelectric testing system (TF2000E; sixACCT).
The dielectric constant and loss were measured in a frequency range of $10^2$–$10^5$ Hz by using an impedance analyzer LCR Hitester (HIoki 3532-50).

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b01626.

Dielic properties as a function of frequency (PDF)

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