Preparation of PZT Thin Film/Ni Particle Composite Magnetoelectric Materials

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Abstract. Lead Zirconium Titanate (PZT) thin film magnetoelectric materials have widely application in controllable sensing and tuneable microwave devices. The PZT film ferroelectric domain was designingly distributed and reversed by using the piezoelectric power response technique. The magnetoelectric composite of PZT film and Ni particle was prepared by the ferroelectric spontaneous polarization separation photogenerated carrier, reduction Ni atom deposition on the PZT thin film ferroelectric positive domain region. The optical morphology, XRD and SEM morphology show that the Ni particles deposited on the PZT film increase first and then become more uniform with the extension of deposition time. The deposition time closely relate to the deposition effect of Ni particles, and the deposition effect is more obvious with time. After the photo-deposition, the surface particles of the unexcited domain film are scattered after the photo-deposition, and the shape of the deposited particles region in which the Ni particles are reduced is substantially similar to the write-domain pattern, and the particle diameter is about 10-20 nm.

1. Introduction
The magnetoelectric composite including single-phase materials and multi-phase composite has important application value in many fields, such as magnetic field detection, electric-magnetic energy conversion, and information storage. The magnetoelectric film composite is easy to integrate with the chip, show good process compatibility of microelectronics and MEMS devices, and have potential applications in the fields of micro-sensor and polymorphic storage, becoming a research focus [1-5].

Self-assembly of metal nanoparticles is the basis for the application of nanomaterials in new electronic devices such as sensors and data storage, as well as catalysts. Magnetoelectric composite materials are self-assembled micro-patterned design and processing of material structure and properties, especially through self-assembly of new micro-patterns, which are of great significance in the application of controllable sensing and tuneable microwave devices. At present, self-assembly methods mainly include solvent evaporation induction self-assembly method, template method, chemical modification method, interface self-assembly method, and self-assembly method using electric field force and magnetic field force induction. The controllable ferroelectric domain structure and photovoltaic effect of ferroelectric thin film materials are particularly suitable for self-assembling metal nanoparticles. The ferroelectric domain structure can be patterned polarized by patterned scanning of the electric field force of the probe, and the ferroelectric domain in the ferroelectric material can be used as a template for self-assembly of the metal nanoparticle by the photo-electric effect to prepare the micro-patterned ferroelectric/magnetic metal. The film/nanoparticle composite play an important role for the applications of material-device integration [6-10].
2. Experiment
Sol-Gel spin method was used to coat the PZT film on 10mm×10mm Pt/Ti/SiO\textsubscript{2}/Si substrate, and the PZT film was annealed at 690 °C to form a perovskite phase, and continue coated and annealed for 4 times.

The PZT film surface morphology and ferroelectric properties were observed using a CypherTM S AFM (atomic force microscope from Oxford Instruments). The ferroelectric hysteresis loop of the PZT film was tested by an atomic force microscope with piezoelectric module. After the sample was fixed with silver paste, a voltage slightly larger than the coercive field was used as the ferroelectric domain inversion voltage, and the domain structure was flipped and polarized. The ferroelectric domain distribution pattern is input into the scanning path of the atomic force microscope with the piezoelectric microscope probe, so that the piezoelectric microscope probe scans the surface of the ferroelectric film according to a given ferroelectric domain distribution pattern, and the ferroelectric thin film pattern area is scanned. The flip voltage is up for the patterned area, and the flip voltage is down for the non-patterned area during polarization operation.

Based on the photo-electric effect, NiCl\textsubscript{2} solution of 10\textsuperscript{-3}mol/L was titrated on PZT film, deposited under simulated solar light source for 30min, 60min and 90min, cleaned with acetone and dried with nitrogen, and Ni particles were reduced and deposited on PZT film to form magnetoelectric composite.

3. Experimental Results and Analysis
The AFM and SEM morphology of the PZT film is shown in figure 1. The flatness of the AFM surface on red line in figure 1 is shown in figure 2. It can be seen from figures 1 and 2 that the PZT multilayer film prepared by the sol-gel spin coating method has smooth surface and good crystallinity, the grain size is about 150 nm, the average flatness is about 4 nm, and the single grain flatness is about 1.5 nm.

![Figure 1. Surface morphology and SEM morphology of PZT film AFM (magnification 10\textsuperscript{5} times).](image-url)

After the ferroelectric domain polarization inversion is completed, the PZT thin film has patterned negative domains and positive domains in the polarization inversion region. With the photovoltaic effect on PZT with ferroelectric effect, Ni\textsuperscript{2+} is reduced to Ni particles, and deposited on the up polarized domain region, as shown in figure 3. Under the photon excitation, PZT will photo-generate electron-hole pairs inside. The electron-hole pairs are separated by spontaneous polarization, and the electrons can effectively migrate to the positive domain face. The Ni\textsuperscript{2+} in the solution are combined with the electrons to be reduced to Ni atom. Then the Ni particles formed by aggregation of Ni atom, and deposit on the positive domain region after the patterned polarization inversion of the PZT film. The band gap width of the PZT film is 3.6 eV, and the energy of the electron excitation should be higher than 4.1 eV (3.6 eV plus 0.5 eV). According to the relationship between the energy of the excited photon and the wavelength, there are must having a wavelength less than 302 nm in the excitation light source. In this
experiment, a simulated solar source containing the wavelength of ultraviolet light is used as the excitation source.

![Figure 2. Flatness curve of the PZT film.](image)

![Figure 3. Schematic diagram of photochemical reduction of Ni particles on PZT film.](image)

The optical topography of PZT/Ni composite material for different NiCl\textsubscript{2} concentrations with illumination time of 60 min are shown in figure 4. Comparing figures 4a, 4b and 4c, it can be found that the deposition with 0.001 mol/L NiCl\textsubscript{2} solution has almost few Ni particles on the surface of the film. Ni particles appeared on the surface of the film with NiCl\textsubscript{2} solution of 0.05 mol/L and 0.01 mol/L, with the distribution was not uniform enough. 0.01 mol/L of NiCl\textsubscript{2} solution is select to conduct follow-up study for it show optimal Ni particle concentration on PZT surface.

![Figure 4. Optical morphology of film surface after deposition of different concentrations of NiCl\textsubscript{2} solution for 60 min.](image)

The surface optical morphology of the film with different deposition times with NiCl\textsubscript{2} concentration of 0.01 mol/L is shown in figure 5. It can be seen from figure 5, that as the deposition time prolongs, the Ni particles deposited on the PZT film increase, and become more uniform.

The local XRD patterns at different deposition times are shown in figure 6. In the figure, the diffraction peak at the diffraction angle of 45° is the Ni phase, indicating that Ni\textsuperscript{2+} is reduced to Ni elemental.

It can be seen from figure 6 that the samples deposited for 30 min and deposited for 60 min showed peaks at around 45°, but the peaks were low. The samples deposited for 90 min showed diffraction peaks at 45° and the peaks were higher. It can be concluded that the deposition time is closely related to the deposition effect of Ni particles, and the deposition effect becomes more obvious with time.
Figure 5. Optical morphology of film surface with different deposition time and NiCl$_2$ concentration of 0.01mol/L.

Figure 6. XRD pattern of PZT film with different deposition time.

SEM morphology and energy spectrum analysis were performed on the surface of the deposited samples, as shown in figures 7 and 8.

By observing the SEM morphology of different deposition times, the Ni particles are deposited less in figure 7a, while the Ni particles are more deposited in figures 7b and 7c.

Comparing figures 8a, 8b, and 8c, we can find that the mass percentage and atomic percentage of Ni element were the highest in the sample deposited for 90 min.

For the PZT film, the “■” shape of the ferroelectric domain was subjected to a patterned polarization inversion of 40 μm*40 μm, and the Ni particles were photochemically reduced in a 0.01 mol/L NiCl$_2$ solution and a simulated sunlight for 90 min. The optical micro-morphology of the PZT film surface before and after photochemical deposition of Ni particles is shown in figure 9.

Figure 7. SEM morphology after deposition of Ni particles on PZT thin films.
Figure 8. Surface particle energy spectrum of Ni/PZT composite film deposited for 30 min, 60 min and 90 min (the insert table is the mass and atomic percentage of Ni element).

It can be seen from figure 9 that in the image before photodeposition, the surface of the film is relatively clean; after photodeposition, there are few scattered particles on the negative polarization region on the upper surface, and the shape of the bright region where the Ni particles are deposited to the positive polarization region on the upper surface. The deposited pattern indicating that Ni particles have been deposited into the positive polarization region.

The XRD pattern after depositing Ni particles on the PZT film is shown in figure 10. The Ni phase diffraction peak indicates that Ni particles were deposited on the PZT film. The SEM microscopy of the PZT film is shown in figure 11. It can be clearly seen that the surface of the PZT film has agglomerated nanoparticles with particle size of about 10-20 nm. Some of the particles maybe fall due to its weak bonding force. The particles were analyzed by energy spectrum, and the results are shown in figure 12. It can be clearly seen from the energy spectrum that Ni element exists. Since the other elements are elements contained in the PZT solution and the substrate, it can be confirmed that the particulate matter on the surface of the PZT film is Ni particles.

Figure 9. Optical microscopy of PZT film surface after photochemical deposition of Ni particles before and after photochemical deposition.

Figure 10. XRD pattern of PZT film deposited with Ni particles.

Figure 11. SEM of PZT film after Ni magnetic particle deposition.

Figure 12. Surface particle energy spectrum and element percentage.
4. Conclusion
The surface of PZT multilayer film prepared by sol-gel spin coating method is smooth and flat, the grain size is about 150 nm, the average undulation is about 4 nm, and the single grain undulation is about 1.5 nm. Using the photovoltaic effect, Ni^{2+} is reduced to Ni particles are deposited to the positive polarization region on the upper surface. With the increase of deposition time, the Ni particles deposited on the PZT film first increased and remained more uniform. The deposition time is closely related to the deposition effect of Ni particles, and the deposition effect is more obvious with time. Scattered randomly distributed particles on the unpolarized region on the upper surface, and the shape of the bright region where the Ni particles are deposited is substantially similar to pattern of the write domain, and the particle diameter is about 10-20 nm.

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