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Silver Doped 0.9PMN-PT-0.1PZT Composite Films for very High Frequency Ultrasonic Transducer Applications

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Abstract

A series of silver doping concentration into the 0.9PMN-PT-0.1PZT (PMN-PT-PZT) films via the composite sol-gel technique were prepared. The crystallographic properties and microstructures of PMN-PT-PZT films with the silver dopant were investigated. Additionally, the effect of silver doping on dielectric and ferroelectric properties was examined. The results show that in general, the dielectric permittivity and remnant polarization increase as the silver doping concentration is increased. The PMN-PT-PZT+ 2.5 mol% Ag film exhibits a dielectric constant of 3,610 at 1 kHz and a remnant polarization of 57.6 $\mu\text{C}/\text{cm}^2$ at room temperature. From this silver doped film, very high frequency ultrasonic needle transducers were fabricated and evaluated. The representative transducer had the center frequency of 225 MHz with a -6 dB bandwidth of 29% (65 MHz) and 62 dB insertion loss. The performance of this transducer is comparable to other composite sol-gel films transducer. The results suggest that this silver-doped PMN-PT-PZT film is a promising candidate as an alternative piezoelectric film for very high frequency transducer applications.

1. Introduction

Much effort has been made to develop piezoelectric materials for wide application in actuators, capacitors and ultrasonic transducers. In the field of ultrasonic imaging, high frequency (> 20 MHz) transducers have been studied intensively for many clinical applications including examination of the skin, anterior segment of the eye and intravascular structures.^{1–3} Because of the need for improved resolution of ultrasonic imaging for biomedical applications, the development of very high frequency (> 100 MHz) ultrasonic transducers is gaining more attention recently. Building such high frequency transducers is challenging and time consuming with traditional machining of bulk piezoelectric ceramics. Piezoelectric thin film technology seems to be a more attractive option to solve this problem in which the transducer fabrication process is simplified. Among different piezoelectric thin film techniques, the composite sol-gel technique is desirable to prepare high quality piezoelectric thin films for making very high frequency (VHF) ultrasonic transducers.^{4–8} This method possesses a number of advantages, i.e., crack-free, cost-effective, flexible, low annealing temperature and good control of film stoichiometry.

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Since lead-based perovskite ceramics provide higher piezoelectric activity than other piezoelectric materials such as ZnO and AlN^{9,10}, they have been widely used in high frequency transducer applications. We recently have reported that it is possible to prepare PMN-PT-PZT composite films with tunable dielectric constant simply by adjusting the composition because the intrinsic dielectric constants of PMN-PT and PZT phases are different.⁷ These materials provide an alternative group of lead-based perovskite ceramics to make very high frequency transducers. Dielectric constant is a key parameter in electrical impedance matching of an ultrasonic transducer to the electronic components. The electrical impedance of the transducer is inversely proportional to the surface area and dielectric permittivity of the piezoelectric material.¹¹ For a progressive need of the miniaturized high frequency ultrasonic transducers and arrays, piezoelectric materials with a relatively higher dielectric constant are more desirable. For example, the surface area size of the transducer that is built using the materials with dielectric constant of 4,000 can be only half of the transducer using the materials with dielectric constant of 2,000. Generally, the compositions of lead-based perovskite ceramics can be customized with additives or other chemical constituents to optimize their functional properties, such as dielectric permittivity, piezoelectric constant and electromechanical property. Previous research has revealed that the dielectric permittivity can be increased with appropriate silver doping of the lead-based ceramics, such as PZT, PMN-PT or PMN-PZT.^{12–15} However, there has been no report on the PMN-PT-PZT ceramics with the silver dopant. We could expect that the dielectric permittivity of the PMN-PT-PZT ceramics should be increased with an appropriate silver doping, which results the practical use in the miniaturization of the transducer and high frequency array applications.

In this work, the PMN-PT-PZT films with different silver doping concentrations were prepared on the platinum-buffered silicon substrate via the composite sol-gel method. The effect of silver doping on the dielectric and ferroelectric properties was examined. A single element ultrasonic transducer was fabricated from this silver doped PMN-PT-PZT film, and its performance was evaluated.

II. Experiment

Silver doped 0.9PMN-PT-0.1PZT films were prepared by the composite sol-gel method. Samples of 0.9PMN-PT-0.1PZT (PMN-PT-PZT)+ x mol% Ag composition were used throughout this study, where x= 0, 1, 1.5, 2, 2.5, 3 and 5. Lead acetate trihydrate (Aldrich Chemical Co., Milwaukee, WI), zirconium n-propoxide (Aldrich Chemical Co.), titanium isopropoxide (Aldrich Chemical Co.), magnesium ethoxide (Aldrich Chemical Co.), and niobium ethoxide (Chemat Technology, Northridge, CA) were used as raw materials with 2-methoxyethanol (Aldrich Chemical Co.) as the solvent to synthesize the precursor sol-gel solution. The composite solution was prepared from PMN-PT as well as PZT powder and precursor solution in mass ratio (powder: solution=1:4), followed by ball milling a mixture of x mol% silver powder (0.5~1 μ m, Alfa Aesar, Ward Hill, MA). Next, the prepared composite solutions were spun at 2000 rpm for 30 seconds on platinum-buffered silicon substrates by a spinner. After spin-coating, each layer was subjected to a two-step pyrolysis sequence to drive out the solvent and decompose organic compounds, one at 200°C for 1.5 min followed by a second step at 400°C for 1.5 min in air. Rapid thermal annealing at 700°C for 1 min was then performed to crystallize the layer. The above procedure was repeated multiple times to achieve the desired thickness. Lastly, the PMN-PT-PZT+x mol% Ag thick films were sintered at 750°C for one hour in a conventional box furnace to increase the film crystallinity.

The crystallographic properties of silver-doped PMN-PT-PZT composite films were analyzed by X-ray diffractometry (XRD, Ultima IV, Rigaku, Tokyo, Japan). The

microstructures of the composite films were observed by field emission scanning electron microscopy (FESEM, S-4800, Hitachi, Tokyo, Japan). The chromium/gold top electrodes with a dimension of $0.5 \times 0.5 \text{ mm}^2$ were sputtered onto the films to evaluate electrical properties. The dielectric properties were measured with an impedance analyzer (Agilent 4292A, Agilent Technologies, Santa Clara, CA). The polarization field (P - E) hysteresis properties were evaluated using a Radiant precision materials analyzer (Radiant Technologies, Albuquerque, NM).

III. Results and Discussion

Figure 1 shows the X-ray diffraction profiles for PMN-PT-PZT+ x mol% Ag composite films on a Pt/Si substrate where x is 0, 1, 1.5, 2, 2.5 and 3. Basically, for the perovskite structure, it has been reported that the addition of silver ion (Ag^+) tends to substitute lead ion (Pb^{2+}) of the perovskite crystal.^{12,13} Because silver ion has similar ionic radius to the lead ion, conspicuous change of lattice constants is not expected. XRD analysis in Fig. 1 reveals that there is no apparent change of lattice constants with the silver addition in the PMN-PT-PZT matrix, which is in agreement with previous reports.^{12–16}

The observed microstructures of PMN-PT-PZT+ x mol% Ag ($x=0, 1$ and 2.5) by FESEM are shown in Figure 2. It can be seen that the density and micromorphology were depended on the silver doping concentration. The undoped PMN-PT-PZT ceramic showed loose micromorphology with relatively small grain size and the existence of more pores. Comparing these silver-doped samples, it was found that higher densification and larger grain size could be achieved with higher concentration of silver dopant. The reason might be that the ceramic oxides reacted with the silver and generated low melting point materials, such as Ag-Pb compounds, which enhanced the diffusion of silver into the ceramics and resulted in the enhancement of densification and the growth of grain size.^{14–16}

The dielectric constant and loss of the silver doped PMN-PT-PZT films were measured by an impedance analyzer. The measured dielectric losses of PMN-PT-PZT+ x mol% Ag films are below 0.06 between 1kHz and 1MHz. Figure 3 shows the measured dielectric constant of different silver doping concentration at 1 kHz. The dielectric permittivity increases as the Ag concentration increases and reaches the maximum value at a doping concentration of 2.5 mol%. Generally, the increase in dielectric constant can be explained in terms of the increase in grain size and densification.^{13–15} However, the dielectric constant decreases when silver concentration above 2.5 mol%, perhaps caused by the increase in second phase consisting of different oxides of lower dielectric permittivity.¹⁷ The order-disorder transition in the B-site lattice is another possible reason responsible for the reduction of dielectric constant.¹³

The ferroelectric hysteresis loops of PMN-PT-PZT+ x mol% Ag ceramics are shown in Fig. 4, and the insert delineates the remnant polarization (P_r) as a function of silver doping concentration. All of the hysteresis loops exhibit the well-saturated and good-symmetrical state, indicating the ferroelectric nature of the pseudocubic phase. It is noted that the remnant polarization is significantly increased with increasing silver doping concentration, owing to the increase of the silver dopant that causes the orientation of the domain to change, enabling the material to have a stronger ferroelectric coupling.¹⁴ This observation suggests that the high concentration of silver dopant contributes to the increase of the polarization.

A single element transducer was fabricated to evaluate the performance of this silver-doped PMN-PT-PZT composite film for ultrasonic transducer application. Here, the 2.5 mol% Ag doped PMN-PT-PZT film which has the highest dielectric constant was selected to make the

representative transducer. After the preparation of $\sim 9 \mu\text{m}$ PMN-PT-PZT+2.5 mol% Ag film, the combination of silicon etching process and conventional transducer technology was used to build the transducer.^{6,11} A representative finished needle transducer is shown in Fig. 5 (a). To induce piezoelectricity in the composite film, the fabricated transducer was poled at 100°C with 120 V in air for 10 minutes. The evaluation of the transducer was tested in deionized water in a pulse-echo arrangement.¹¹ The measured pulse-echo response and normalized frequency spectrum are given in Fig. 5 (b), where the center frequency is 225 MHz and -6 dB bandwidth is 29% (65 MHz). Additionally, the measured insertion loss is 62 dB. The silver-doped PMN-PT-PZT composite films exhibit good dielectric and ferroelectric properties with comparable transducer's performance to other reported composite sol-gel films transducers (see Table I). The results demonstrate the capability of this silver-doped PMN-PT-PZT thick film for very high frequency transducer applications.

IV. Conclusions

The silver-doped PMN-PT-PZT films with a series of doping concentration were prepared using the composite sol-gel method. The effect of silver doping in crystallized structure, micromorphology, dielectric and ferroelectric properties is described. The PMN-PT-PZT +2.5 mol% Ag film exhibits a high dielectric constant of 3,610 (at 1 kHz) and a remnant polarization of $57.6 \mu\text{C}/\text{cm}^2$ at room temperature. A high frequency single element needle transducer was built using this $\sim 9 \mu\text{m}$ silver-doped PMN-PT-PZT film. The measured center frequency was 225 MHz with 29% bandwidth and 62 dB insertion loss. The results imply that this silver-doped PMN-PT-PZT film is a promising candidate as an alternative piezoelectric film for very high frequency ultrasonic transducer applications.

Acknowledgments

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Fig.1.

X-ray diffraction patterns of the samples with different Ag doping concentrations: (a) 0 mol %, (b) 1 mol%, (c) 1.5 mol%, (d) 2 mol%, (e) 2.5 mol% and (f) 3 mol%.

Fig.2. Scanning electron micrographs of the microstructures of PMN-PT-PZT+ x mol% Ag films while x is (a) 0, (b) 1 and (c) 2.5.

Fig.3. Dielectric constant of Ag-doped PMN-PT-PZT films with different silver concentration (x mol%) as a function of applied frequency measured at 1 kHz.

Fig.4. The ferroelectric hysteresis loops of PMN-PT-PZT+ x mol% Ag ceramics where x is 0, 1, 1.5, 2, 2.5, 3 and 5. The insert: The remnant polarization (P_r) as a function of silver doping concentration.

Fig.5.

(a) A photograph of the fabricated PMN-PT-PZT+2.5 mol% Ag needle transducer, (b) Measured pulse-echo waveform (solid line) and normalized frequency spectrum (dashed line).

Table I

Measured properties and performance of composite sol-gel films VHF transducers.

Transducer	f_c (MHz)	BW (%)	P_r ($\mu\text{C}/\text{cm}^2$)	e_r (at 1 kHz)
9 μm PMN-PT-PZT+2.5 mol% Ag	225	29	58	3610
10 μm PZT ⁴	156	50	42	1925
12 μm PMN-PT ⁵	110	64	30	3326
9 μm PMN-PT-PZT ⁷	200	38	27	2534
5 μm KNN/BNT ⁶	193	34	24	848