Amorphous-nanocrystalline lead titanate thin films for dielectric energy storage

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Many high permittivity crystalline dielectric thin films have a low breakdown strength, which is unfavorable for dielectric energy storage devices. In contrast, many amorphous linear dielectrics have much lower permittivities but larger breakdown strengths. Here, composite thin films with nanocrystalline particles in an amorphous matrix were explored to increase the stored energy density of dielectrics. For this purpose, thin films of lead-rich lead titanate, Pb1.1TiO3.1, were fabricated via chemical solution deposition and heat-treated at temperatures ≤400°C. Transmission electron microscopy indicated the presence of dense lead oxide nanocrystals in an amorphous lead titanate network. The films exhibit a relative permittivity of 32.6 and a low dielectric loss of 0.0008. The leakage current is approximately 10⁻⁸ A/cm², with a DC breakdown strength between 2 and 3 MV/cm. The 1 kHz breakdown strength exceeds 5 MV/cm. At an electric field of 5 MV/cm and a measurement frequency of 1 kHz, the maximum in energy storage density was ~28 J/cm³. These properties suggest that nanocomposite Pb1.1TiO3.1 films may be a suitable candidate for integration into energy storage devices.

1. Introduction

Advances in renewable energy sources and hybrid/electric vehicles are dependent on the development of capacitive materials with both high energy and high power storage densities. For a system to simultaneously possess a high energy and high power storage density, batteries and capacitors are typically used in tandem to mitigate the problems associated with fluctuating power output from renewable energy sources. Hybrid/electric vehicles benefit from the use of battery and capacitor electrical systems, which ensure the power, lifetime, and reliability of the vehicle. Typical capacitors have a high power density and a relatively small energy storage density, while batteries are responsible for maintaining a high energy storage density for the system. One approach to the optimization of energy storage devices used in electronic systems is to increase the energy storage density of dielectric capacitive materials.

Energy storage density is a function of both the dielectric constant (induced polarization) and breakdown strength of a material. The three parameters are related by Eq. (1), which relates the stored energy density to the induced polarization and electric field:

\[ J = \int_0^{P_{\text{max}}} EdP. \]  

where \( J \) is the energy storage density, \( E \) is the electric field applied to the material, \( P \) is the polarization induced in the dielectric, and \( P_{\text{max}} \) is the induced polarization at the highest applied electric field. Most materials that are used for energy storage applications have either a high permittivity and relatively low breakdown strength or a comparably low permittivity and higher breakdown strength, as is the case for some polymers and amorphous materials. The challenge is to simultaneously achieve a moderately high permittivity with high breakdown strength, while maintaining a low loss tangent under high electric fields.

Figure 1 (after Sherrit) shows the energy storage density of ideal (a) linear dielectric, (b) ferroelectric, (c) relaxor, and (d) antiferroelectric materials; the shaded area of the polarization-electric field hysteresis curve is the energy storage density. Ferroelectric materials generally have high permittivities (often on the order of 1000), but the hysteresis contributes to higher energy losses. Many ferroelectric materials are further limited by their moderate breakdown strengths, which are often below 1 MV/cm. Relaxor ferroelectrics offer high permittivity values, but much slimmer polarization-electric field hysteresis loops than most normal ferroelectrics, which reduces energy loss from the material. Thus, ferroelectric relaxors have the potential for high energy storage densities, provided that the breakdown strength of these materials is sufficiently high. Antiferroelectric materials are also promising due to a zero value for remanent polarization. Linear dielectrics are a topic of intense research efforts due to the potential breakdown strength-permittivity compromise they offer. In addition to relatively high breakdown strengths and moderate permittivity values (usually less than 100), linear dielectrics exhibit low loss tangents. An increase in the breakdown strength of linear dielectrics is critical in the improvement of this material class for their use in energy storage devices. Several example thin film materials and their energy storage densities are provided in Table 1; the processing temperature used for each film is also provided.

The combination of two or more materials with desired properties, such as high dielectric constant and high breakdown...
strength, could enable a composite thin film material with an energy storage density superior to its constituents. \textsuperscript{12} Reported examples usually consist of ceramic particles in a polymer matrix. The ceramic particles provide a component with a higher dielectric constant, while the polymer matrix is intended to provide high breakdown strength. \textsuperscript{31} The ratio between the two materials must be carefully controlled; if an insufficient concentration of particles is used, the material will not have a large dielectric constant, and if the concentration of particles is too high, a pathway for current through the material will be introduced. \textsuperscript{12,13} For example, at an optimized volume fraction of 22.5\% barium titanate powder dispersed in a silicone elastomer (Sylgard184\textsuperscript{®}, Dow Corning, Midland, MI) the permittivity of the composite approximately doubled, while the breakdown strength of the material remained approximately equal to that of the pure elastomer. \textsuperscript{12}

It may also be possible to utilize a stiff amorphous matrix in the composite to increase the breakdown strength of the resulting thin film material. Here, high energy density dielectrics for energy storage which could be processed at low temperatures were pursued by making nanocomposite thin films of a medium permittivity crystalline material in an amorphous matrix. The intent was to use the amorphous host to increase the breakdown strength by eliminating the possibility of a breakdown pathway forming along grain boundaries. \textsuperscript{13} Furthermore, amorphous films are often smoother than polycrystalline films, thus minimizing electric field intensification at asperities. \textsuperscript{14} The primary breakdown mechanisms for amorphous materials are typically residual ionic impurities from film processing or small, randomly distributed voids in the material that present a weak pathway or discharge channel. \textsuperscript{15} Amorphous and semicrystalline materials may also exhibit a lower dielectric loss \textsuperscript{15} and leakage current \textsuperscript{13} than their fully crystalline counterparts. Although the dielectric constant of amorphous materials is lower than that of crystalline materials, a high energy storage density may be obtained if this reduction in permittivity is compensated by an enhancement in breakdown strength. For example, Sethi et al. \textsuperscript{16} achieved breakdown strengths as high as 4 MV/cm and an energy density of 14 J/cm\textsuperscript{3} with amorphous tantalum pentoxide films (the relative permittivity was \~{}25).

The use of amorphous materials is advantageous because the high temperatures required to produce crystalline thin films limit possible substrates to materials with high melting points, preventing the use of polymeric substrates that may have uses in flexible electronics applications. Furthermore, low temperature thin film processing allows for fabrication of embedded capacitors and is more energy efficient than high temperature crystallization steps. In this work, nanocomposite lead titanate films were deposited via chemical solution deposition at temperatures below 400°C, without a vacuum system or stringent oxygen partial pressure control. Although crystalline lead titanate is well known, the properties of amorphous, undoped lead titanate have not been thoroughly investigated. Crystalline lead titanate has an intrinsic polycrystalline dielectric constant of approximately 75 \textsuperscript{17} and a leakage current of approximately 10\textsuperscript{−6} A/cm\textsuperscript{2}. \textsuperscript{18} Amorphous lead titanate has a dielectric constant between 20 and 30. \textsuperscript{19}

The objective of this paper is to characterize nanocomposite, lead-rich lead titanate, Pb\textsubscript{1.1}TiO\textsubscript{3.1} with lead oxide crystallites in an amorphous lead titanate matrix, and determine its dielectric properties, particularly its suitability for energy storage device applications.

2. Experimental procedure

Nanocrystalline/amorphous composite, lead-rich lead titanate, Pb\textsubscript{1.1}TiO\textsubscript{3.1}, thin films were prepared on platinized silicon wafers via a chemical solution deposition method. Inclusion of excess lead in the precursor solution is intended to promote the formation of lead oxide nanocrystallites in the amorphous lead titanate matrix of the final film. Ten percent excess lead acetate trihydrate

Table 1. Energy storage densities and processing temperatures of several ceramic and polymer thin film materials

| Material | Energy storage density J/cm\textsuperscript{3} | Maximum processing temperature/°C |
|----------|----------------------------------|--------------------------------|
| PLZT\textsuperscript{15} | 22 | 625 |
| PLZST\textsuperscript{27} | 13.7 | 700 |
| 0.6 BaTiO\textsubscript{3}–0.4 BiScO\textsubscript{3}\textsuperscript{28} | 13 | 450–750 |
| PVDF\textsuperscript{29} | 24 | 110 |
| Nanocomposite PVDF\textsuperscript{30} | 19 | 200 |

PLZT, lead lanthanum zirconate titanate; PLZST, lanthanum-doped lead zirconate stannate titanate; PVDF, polyvinylidene fluoride.
(Sigma-Aldrich, St. Louis, MO) was used during solution preparation. Solutions were prepared using an inverted mixing order synthetic route\(^{20,21}\) to avoid the use of 2-methoxyethanol. The precursors used were lead acetate trihydrate and titanium isopropoxide (Sigma-Aldrich). The solvents used were acetic acid (≥99.7%, Sigma-Aldrich) and methanol (Sigma-Aldrich). Lead acetate trihydrate and titanium isopropoxide were combined in acetic acid, and then stirred on an 85°C hotplate for approximately ten minutes to allow for chelation of the central metal atoms by acetyl ligands. Following this reaction step, the mixture was stirred for an additional ten minutes. Methanol and acetic acid were added to reach a final molarity of 0.4 M, and the solution was stirred for ten minutes to homogenize it. The final solution contained a 3:2 ratio of acetic acid to methanol.

To deposit thin films, the precursor solution was diluted with acetic acid to 0.2 M before spin coating at 3500 rpm for 30 s on a platinum-coated silicon wafer [Pt (100 nm)/Ti (20 nm)/SiO\(_2\) (500 nm)/Si, NOVA Electronic Materials, Flower Mound, TX]. The substrate was placed on a hotplate to dry at 175°C for one minute, followed by a one minute pyrolysis step at 350°C to remove organics and promote densification in the film. The film was heat treated in a rapid thermal anneal system (RTP-600S, Modular Process Technology Corp., San Jose, CA) for two minutes. The annealing temperature was varied to determine the crystallization temperature and the optimal processing temperature for nanocomposite lead titanate. Most films were annealed at 400°C. This process of spin casting followed by three sequential heat treatments was repeated several times to build up film thickness. The film thickness was typically between 300 and 400 nm after six layers were deposited. The processing route is shown schematically in Fig. 2.

| Titanium iso-propoxide + Acetic Acid | Lead acetate trihydrate + Acetic Acid |
|-------------------------------------|--------------------------------------|
| Stir at 80°C C                       | Repeat once                           |
| Add methanol and acetic acid        | Repeat to thickness                   |
| Dilute to 0.2 M                      |                                       |
| Spin at 3500 rpm for 30 s            |                                       |
| Dry at 175°C C for 1 min             |                                       |
| Pyrolyze at 350°C C for 1 min        |                                       |
| Anneal                               |                                       |

Fig. 2. Flowchart for the processing of nanocomposite thin films of lead titanate. Solutions were prepared using an inverted mixing order synthetic route, spin cast onto a substrate, and thermally treated in three steps.

The permittivity and dielectric loss tangent of the nanocomposite lead titanate films were measured with an LCR meter (Hewlett-Packard 4284A Precision, Agilent Technologies, Inc., Palo Alto, CA) at an AC oscillation voltage of 0.03 V and a frequency of 1 kHz. Polarization-electric field behavior was determined using a multiferroic analyzer (Precision Multiferroic, Radiant Technologies, Inc., Albuquerque, NM) with a hysteresis period of 1 ms. Leakage current measurements utilized a pA meter (Hewlett-Packard 4140B pA meter, Agilent Technologies, Inc.) with a step size of 1 V and a soak time of 90 s.

3 Results and discussion

3.1 Phase identification and film structure

A crystalline film was deposited using the method from Fig. 2. To fully crystallize the material while minimizing the volatility of excess lead from the film, the film was annealed in the rapid thermal annealing system at 550°C for two minutes. The resulting XRD pattern is shown in Fig. 3(a). The diffraction peaks are consistent with the perovskite structure of crystalline lead titanate (PDF# 00-006-0452, 1955) along with peaks from orthorhombic lead oxide (PDF# 00-035-1482, 1984) at 29 values of 28.7° (111) and 59.5° (222). Figure 3(b) shows the XRD pattern of the lead titanate films that were annealed at 400°C for two minutes. These films are XRD amorphous; no diffraction peaks besides those attributable to the substrate are present in the spectrum. There is an amorphous hump between 2θ values of approximately 26 and 33°, the degree range within which the strongest lead oxide peak lies, corresponding to the (111) diffraction plane. The surface microstructures are smooth, without any noticeable topography, which is in agreement with their amorphous state as confirmed by XRD.

Figure 4 shows images obtained from transmission electron microscopy, which confirm the nanocomposite nature of the films. The cross-sectional transmission electron microscopy image of Fig. 4(a) depicts a dense film atop a crystalline platinum substrate. The columnar grain structure of the underlying platinum can be seen, while the film consists of isolated nanocrystals randomly...
distributed throughout an amorphous network. The film-substrate interface is smooth, minimizing the electric field amplification associated with non-uniformities. The high-magnification transmission electron microscopy image of Fig. 4(b) verifies the formation of dense, isolated nanocrystals in an amorphous network. This is further verified in the inset image of (b), which shows diffraction points within a diffuse ring.

3.2 Film properties

Figure 5 shows the polarization-electric field hysteresis loop for nanocomposite lead titanate swept to an electric field of 1 MV/cm. The loop shows nanocomposite lead titanate to be a linear, low loss dielectric. The dielectric constant is 32.6, and the dielectric loss of the film is approximately 0.0008, indicating that there is little charge trapping and energy loss in the material at applied electric fields of 1 MV/cm. As the material is subjected to higher electric fields, the dielectric loss of the film increases, widening the loops significantly.

The energy and power storage densities for each loop in Fig. 6, spanning an applied electric field range from 2 to 5 MV/cm, are given in Table 2. The power density of the film was calculated using Eq. (2):23)
The power storage density of the dielectric loss in the film of the material increases. Although the energy storage density of the film improves with applied electric field despite the increase in loss, the power storage density of the films decreases.

Table 2. Energy storage density of nanocomposite lead titanate

| Maximum electric field/MV.cm⁻¹ | Energy storage density ± standard deviation/J.cm⁻³ | Power storage density/MW.cm⁻³ |
|---------------------------------|-----------------------------------------------|-----------------------------|
| 2.0                             | 5.9 ± 0.1                                     | 21.1                        |
| 2.5                             | 8.8 ± 0.2                                     | 10.6                        |
| 3.0                             | 12.6 ± 0.2                                    | 5.0                         |
| 3.5                             | 16.8 ± 0.1                                    | 2.5                         |
| 4.0                             | 20.7 ± 0.2                                    | 1.2                         |
| 4.5                             | 24.9 ± 0.3                                    | 0.43                        |
| 5.0                             | 28.4 ± 0.1                                    | 0.19                        |

Fig. 7. Energy and power storage density as a function of applied electric field. As the material is swept to higher electric fields, the dielectric loss in the film increases. Although the energy storage density of the film improves with applied electric field despite the increase in loss, the power storage density of the films decreases.

Fig. 8. Polarization-electric field hysteresis loop for nanocomposite lead titanate at a maximum applied electric field of 4.5 MV/cm. At this electric field, the films attain their maximum energy storage density of ~28 J/cm³.

\[ P = \frac{\pi f J}{\tan \delta} \]  

where \( P \) is power density, \( f \) is the frequency at which \( \tan \delta \) is measured, \( \tan \delta \) is the dielectric loss of the film under the applied electric field at which \( J \) is calculated, and \( J \) is energy storage density. A plot of both energy and power density as a function of applied electric field are given in Fig. 7.

Figure 8 shows the polarization-electric field hysteresis loop for a film that was swept to a maximum applied electric field of 5 MV/cm, the electric field for which nanocomposite lead titanate achieves its maximum energy storage density. The area that was calculated to determine the energy storage density is shaded in Fig. 8. At this electric field, the energy storage density of the film is approximately 28 J/cm³. The high breakdown strength of the material can likely be attributed to the amorphous lead titanate matrix of the film. The lack of structural periodicity of the amorphous network and the isolated, randomly distributed lead oxide nanocrystals do not present a conduction pathway through the film. The moderately high permittivity of the film is enhanced by the presence of lead oxide nanocrystals. Figure 9 shows the temperature dependence of the energy storage density. The moderate decrease in the energy storage density at temperatures up to 150°C is attributable to the decrease in breakdown strength of the material at increased temperatures. As film temperature increases, the conductivity through the film will also increase, promoting breakdown. At temperatures beyond 150°C, the energy storage density of the film drastically decreases.

The energy storage density of nanocomposite films of lead titanate slightly exceeds that of most other ceramic and composite dielectric thin films previously reported. The high breakdown strength of these films, coupled with the moderate relative permittivity of the nanocomposite, resulted in a high energy storage density. It is possible that further improvements could be achieved in the nanocomposite lead titanate films via reduction of the dielectric loss at large applied electric fields. Among the avenues that should be explored are further densification of the film, and minimization of charge injection into the film. Finally, the dielectric properties of the material may be further improved by doping with niobium or lanthanum to lower the dielectric loss of lead titanate, and potentially increasing the energy storage density of the films.

Figure 10 shows the leakage current density as a function of electric field for nanocomposite lead titanate films. The leakage current for this material is extremely low, which was attributed to the amorphous matrix of the film. As seen in Fig. 10, the DC breakdown strength of the film is approximately 2.5 MV/cm. Since these films were processed at the relatively low annealing temperature of 400°C, it is possible to integrate these materials into displays or capacitors on either polyimide or glass substrates.

4. Conclusions

Nanocomposite, lead-rich lead titanate (Pb₃₋₁TiO₃₋₃) thin films were investigated for their potential in energy storage device...
applications. The films were fabricated via chemical solution deposition using a precursor solution that was synthesized with an inverted mixing order process. The films are smooth, uniform, and dense. Transmission electron microscopy shows the nucleation of isolated nanocrystals of lead oxide in an amorphous lead titanate network. The nanocomposite has a permittivity of 32.6 and a low loss tangent of 0.0008. The DC breakdown strength of the material is approximately 2.5 MV/cm, while the AC breakdown strength of the material exceeds 5 MV/cm. The material exhibits low leakage currents (on the order of $10^{-4}$ A/cm²), and a high energy storage density of $\sim 28$ J/cm³. The maximum energy storage density occurs when the material is subjected to an electric field of 5 MV/cm, and is limited by dielectric loss in the film. Nanocomposite lead titanate thin films may be suitable for use in energy storage devices.

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