Enhanced dielectric properties and energy storage density of Mg-doped SrTiO₃ nanowire films

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Abstract

To improve dielectric properties of SrTiO₃-based materials and meet their development requirements in various scientific and technology fields, Mg-doped SrTiO₃ nanowire films (with 0, 0.5, 1, 1.5 and 2 mol% Mg) were fabricated by liquid phase deposition (LPD) process. The results showed that structural and dielectric properties of the prepared samples can be effectively affected by Mg doping. Thus, the SrTiO₃ nanowire film doped with 1.5 mol% Mg has high dielectric constant of 594.2, a low dielectric loss of 0.0167 and the highest breakdown strength of 463.1 kV/cm at 1 kHz, therefore resulting in a high energy density of 5.64 J/cm³, which is about 3.9 times higher than that of the pure SrTiO₃ nanowire films (1.44 J/cm³). Based on findings in this research, it was shown that improvement of dielectric properties of SrTiO₃ ceramic systems can be obtained with formation of one-dimensional structures and selecting reasonable Mg content for doping.

Keywords: Mg-SrTiO₃ nanowire films, liquid phase deposition, dielectric properties, energy storage density

I. Introduction

Nowadays, the development of advanced materials and efficient methods for electrical energy storage is an essential topic of research due to their potential applications in solar cells, fuel cells, batteries and capacitors [1]. Among them, dielectric capacitors are ubiquitous components in modern electronic devices and power systems that possess high power density and ultrafast charge-discharge rate [2]. However, the application of conventional dielectric capacitors is extremely restricted by the low energy storage density. To achieve high energy storage performance, two factors are crucial, i.e. high electric displacement or relative dielectric constant and high electric breakdown strength. Furthermore, low dielectric loss also plays an important role in practical applications [3]. Thus, the study of novel dielectric materials with improved energy storage efficiency has always been at the centre of interest of researchers in high-voltage capacitors.

SrTiO₃-based dielectric ceramics with a linear characteristic, intrinsically containing medium-high dielectric constant, low dielectric loss, high energy storage performance, low cost, excellent thermal stability and high breakdown strength are considered as one of the most promising candidate materials for energy storage applications [4–7]. Many efforts have been dedicated by the means of tailoring the material structure thus far to improve the energy storage density of SrTiO₃ dielectrics based on increasing dielectric constant and breakdown strength [8–10]. Ion substitution, multi-component composites and high aspect ratio one-dimensional (1D) ceramics provide practical and effective approaches to realize the high-performance SrTiO₃ [3,11]. Dielectric properties of SrTiO₃ can be adjusted by ion substitution at A or B positions of SrTiO₃ ABO₃ perovskite structure [12,13].

Mg dopant is widely used to modify the structure and properties of SrTiO₃. For instance, Tkach et al. [14] investigated the effect of Mg doping on the structural and dielectric properties of SrTiO₃ ceramics. They found that Mg solid solubility is restricted to less than 1 and 15 mol% for A- and B-site occupancy, respectively. Yao et al. [15] found a relative permittivity of ~280, low dielectric loss of about 0.001 at 1 kHz, and energy storage density of 1.86 J/cm³ with good energy efficiency of 89.3% in optimal composition of 0.01 mol% Mg-doped SrTiO₃.
On the other hand, it is well known that 1D structures, such as nanowires, nanorods and nanotubes, can effectively improve the dielectric properties of ceramics compared to their corresponding nanoparticles. This is attributed to the larger dipolar moment in ferroelectrics compared to their corresponding nanoparticles. This aspect-ratio nanowires demonstrated superiority in improving dielectric constant and breakdown strength, thereby enhancing the energy density of nanocomposites.

Several methods are utilized to fabricate 1D SrTiO$_3$, including sol-gel [18], hydrothermal [3], self-templated synthesis [19] and template-based synthesis [20]. The template-based synthesis methods can easily produce 1D SrTiO$_3$ arrays with a uniform diameter at low temperatures. Therefore, in this approach, it is necessary to provide membranes as a template. Alumina and polycarbonate membranes are the most commonly used for synthesis of 1D nanostructured arrays. Both templates are very convenient to use during the growth of the 1D arrays by various growth mechanisms, but each type of template also has a few disadvantages. The advantage of using polycarbonate as the template is related to its rigidity and strong resistance to high temperatures. The largest limitation is that the polycarbonate’s lack of flexibility, especially during heating and removal of the template, may damage the nanotubes/nanowires. These factors would result in broken and deformed nanowires. The advantage of using an anodic aluminium oxide (AAO) membrane as the template is its rigidity and strong resistance to high temperatures, which allows the 1D nanostructures to be completely densified before its removal [21]. This would lead to a larger surface area of fairly free-standing, uniform parallel and unidirectionally-aligned arrays, which make the AAO membrane an ideal template to prepare ordered nanowire arrays. There are different template-assisted methods of which liquid phase deposition (LPD) process is a low-cost and environmentally-friendly method to form metallic oxides from the aqueous solution of a metal-fluoro complex ion, which can be slowly hydrolysed by adding boric acid or Al metal [8]. However, only a few reports on LPD deposition of SrTiO$_3$ nanowire films have been published.

Herein, SrTiO$_3$ nanowire films with different levels of Mg doping were successfully prepared via the LPD process. The effects of Mg contents on structural and dielectric properties of the SrTiO$_3$ nanowire films to achieve high dielectric constant, low loss dielectric, high breakdown strength and simultaneously high energy storage efficiency were evaluated in detail.

II. Experimental procedure

Anodic aluminium oxide (AAO) membranes (Anodisc; Whatman Inc.) with a diameter of 25 mm and a nominal pore size of about 100 nm were used as the starting template material. The SrTiO$_3$ nanowire films were fabricated in the pores of the AAO membranes by LPD process. In this manner, a 0.1 mol/l treatment solution was prepared by dissolving (NH$_4$)$_2$TiF$_4$ (Sigma-Aldrich, 99.99%) as a metal-fluoro complex in deionized water. In another glass beaker, 0.11 g Sr(CH$_3$COO)$_2$ (Alfa, 98%) was dissolved in 5 ml deionized water by stirring constantly. Two aqueous solutions were mixed in a molar ratio of 1:1. Then Mg, as the dopant was introduced from magnesium acetate (Alfa, 98%) with amount of 0, 0.5, 1, 1.5 and 2 mol% to obtain solution and continually stirred for 30 min. Subsequently, the AAO membranes were vertically immersed into the aqueous solution and maintained for 4 h at room temperature. After deposition, the membranes were taken out from the solution and rinsed with distilled water and ethanol. To remove the AAO membranes, the samples were placed in an H$_3$PO$_4$ solution for 10 min, followed by rinsing in ethanol and water till it was free from the H$_3$PO$_4$ solution. Finally, the prepared nanowire films were heat-treated at 750 °C for 2 h to enhance the crystallization. Figure 1 illustrates a schematic diagram of the fabricating procedure for Mg-doped SrTiO$_3$ nanowire films.

Crystal structure of the SrTiO$_3$ nanowire films was characterized by Panalytical X’Pert PRO X-ray diffraction (XRD; CuK$_a$ radiation) equipped with High Score software. Scanning rate and scanning range were 2°/min and 20–70°, respectively. To examine the basic functional groups and chemical bonding in the synthesized compounds, FTIR spectra were obtained on a Nicolet Magna-IR 550 spectrometer in the frequency range of 400–4000 cm$^{-1}$. The products were mixed with KBr powder and compressed to a thin pellet. Sup-

Figure 1. Schematic representation of fabrication process for the Mg-doped SrTiO$_3$ nanowire films
supplementary Raman scattering spectra were recorded with Raman-532-Ci spectrometer (Avantes, The Netherlands) in the spectral range of 100–1000 cm\(^{-1}\). Nd-YAG laser beam with a wavelength of 523 nm was used as the excitation source. A TESCAN MIRA3 field emission-scanning electron microscopy (FE-SEM) equipped with energy-dispersive X-ray spectroscopy (EDS) was employed to study morphology and corresponding elemental distribution in the SrTiO\(_3\) nanowire films. Dielectric properties of the samples, such as dielectric constant (\(\varepsilon_r\)) and dielectric loss (\(\tan\delta\)), were measured with the Hioki IM3536 LCR meter in the frequency range from 1 to 1000 kHz. Before the dielectric measurements, the nanowire films were sputtered with a silver as an electrode on both sides. The real part of \(\varepsilon_r\) was calculated from the capacitance using the following equation [1]:

\[
\varepsilon_r = \frac{C \cdot d}{\varepsilon_0 \cdot A}
\]

where \(C\) is the parallel capacitance, \(d\) is the thickness of the film, \(A\) is the area of the capacitor and \(\varepsilon_0\) is the absolute dielectric constant of free space (8.85\(\times\)10\(^{-14}\) F/cm).

Dielectric breakdown strength measurements were carried out at room temperature in silicone oil as an insulating medium to avoid arcing. Six breakdown trials were tested to evaluate the breakdown strength through the Weibull distribution function due to the randomness of the dielectric breakdown voltage.

### III. Results and discussion

Figure 2 shows XRD patterns of the SrTiO\(_3\) nanowire films with different Mg contents calcined at 750 °C for 2 h. It can be observed that the diffraction peaks at 2\(\theta\) of 22.8°, 32.4°, 40°, 46.5°, 57.8° and 67.8° are indexed to (100), (110), (111), (200), (211) and (220) planes of SrTiO\(_3\) with cubic perovskite structure (JCPDS No. 073-0661) [3]. This confirms presence of a single phase of SrTiO\(_3\) with no additional peaks related to magnesium oxide or other impurity phases when the Mg content is less than 1.5 mol\%. This confirms that Mg ions were incorporated into the SrTiO\(_3\) lattice to form homogeneous solid solutions. Peak shifting toward higher diffraction angles was observed with the increasing Mg contents, as shown in 31–33° 2\(\theta\) range. This shift suggests the enhancement of Mg incorporation into the unit cell of the perovskite structure. This phenomenon can be explained by the difference between ionic radii of the host and dopant ions. The ionic radius of Mg\(^{2+}\) ion (1.1 Å) is smaller than those of Sr\(^{2+}\) ion (1.4 Å) [4]. Therefore, the substitution of Mg\(^{2+}\) ions on the CN12 Sr-site leads to the shrinkage and decreased lattice parameter in the SrTiO\(_3\) lattice. The results are in agreement with those obtained by Okhay et al. [4] and Tkach et al. [14].

When Mg content is 2 mol\%, the weak diffraction peaks at the angles of 43° and 62.3° corresponding to MgO 200 and 220 reflections (JCPDS No. 01-1235) appeared, which indicates the presence of MgO in the SrTiO\(_3\) compound. It was also found that the relative intensity of diffraction peaks decreases with increasing Mg content, demonstrating lower degree of crystallization.

The average crystallite size and lattice parameter (\(a\)) of samples were estimated using the Rietveld refinement analysis [22] and the obtained values for the pure and Mg-doped SrTiO\(_3\) nanowire films calcined at 750 °C for 2 h are given in Table 1. It is quite clear that the average crystallite size and the lattice parameter decrease by increasing the Mg content, which may be due to the substitution of Mg\(^{2+}\) ions in the host SrTiO\(_3\) lattice.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Crystallite size [nm]</th>
<th>Lattice parameter [Å]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure SrTiO(_3)</td>
<td>22.1</td>
<td>3.910</td>
</tr>
<tr>
<td>SrTiO(_3)-0.5% Mg</td>
<td>21.6</td>
<td>3.903</td>
</tr>
<tr>
<td>SrTiO(_3)-1.0% Mg</td>
<td>21.0</td>
<td>3.899</td>
</tr>
<tr>
<td>SrTiO(_3)-1.5% Mg</td>
<td>20.4</td>
<td>3.896</td>
</tr>
<tr>
<td>SrTiO(_3)-2.0% Mg</td>
<td>19.6</td>
<td>3.890</td>
</tr>
</tbody>
</table>

Table 1. Crystallite size and lattice parameter of the pure and Mg-doped SrTiO\(_3\) nanowire films calcined at 750 °C/2 h

Figure 3 displays FTIR spectra of the doped SrTiO\(_3\) nanowire films uncalcined and calcined at 750 °C for 2 h. The broad peak around 3400–3500 cm\(^{-1}\) can originate from the stretching vibrations of OH groups, indicating the presence of adsorbed water and ethanol molecules on the sample surface. The peak located around 1640 cm\(^{-1}\) is associated to OH groups and one to 1422 cm\(^{-1}\) may be assigned to the stretching vibrations of carbonate groups, i.e. CO\(_3^{2-}\) [23]. It can be seen (Fig. 3b) that the intensity of these bands extremely decreases after calcination at 750 °C. The peak located at 855 cm\(^{-1}\) was attributed to the TiO\(_6\) octahedron bending vibration [24]. The broad absorption peaks located below 800 cm\(^{-1}\) are due to the Sr–Ti–O stretching modes, indicating the formation of SrTiO\(_3\) [25]. No additional peaks appeared at this wavelength region when Mg con-

![Figure 2. XRD patterns of SrTiO\(_3\) nanowire films doped with different Mg contents calcined at 750 °C for 2 h](image-url)
tent was less than 1.5 mol%, evincing that doped Mg$^{2+}$ entered into the framework of SrTiO$_3$. When Mg content was 2 mol%, the characteristic absorption peak between 500–570 cm$^{-1}$ for MgO was observed [26]. The aforementioned results exhibited that the Mg solubility limit in SrTiO$_3$ is between 1.5 and 2 mol%, which is in accordance with the XRD results.

Raman spectroscopy is one of the tools to study the crystal structure and order-disorder present in a material. The room-temperature Raman spectra of the pure SrTiO$_3$ and Mg-doped SrTiO$_3$ nanowire films calcined at 750°C for 2 h are shown in Fig. 4. It is well known that SrTiO$_3$ with an ideal cubic perovskite structure permits the second-order scattering and no first-order Raman-active vibration frequencies are allowed because the optical phonon moment at the centre of the Brillouin zone is zero. However, the Raman spectra show two broader peaks located at 200–500 cm$^{-1}$ and 600–800 cm$^{-1}$, due to the presence of the second-order Raman scattering [24]. Four first-order peaks at approximately 176, 263, 540 and 794 cm$^{-1}$ are identified, which can correspond to TO$_2$, TO$_3$, TO$_4$, and LO$_4$ phonon modes, respectively [27]. The appearance of such forbidden polar modes in Raman spectra is actually possible when the crystal symmetry is broken due to several factors such as the presence of defects, oxygen vacancies or incorporated impurities in the crystal lattice and strain effects from the lattice mismatch and grain boundaries [28]. The strong peaks at 176 and 540 cm$^{-1}$ correspond to the transverse optical polar mode (TO$_2$) representing the Sr/Mg motion concerning the TiO$_6$ octahedron and polar axe mode (TO$_4$) originating from the bending of the octahedron, respectively [5]. The activation of the TO$_2$ and TO$_4$ polar states suggests an increase in the degree of polar distortion by Mg doping. The weak peak at 264 cm$^{-1}$ corresponds to the transverse optical non-polar mode (TO$_3$), while the peak centred at 800 cm$^{-1}$ refers to the stretching mode (LO$_4$ mode), which arises due to the induced local disorder and variation of the cations in the SrTiO$_3$ [24]. It is observed that with an increasing Mg content, intensity of the Raman scattering peaks increases and becomes broader. Similar results were reported by Okhay et al. [4] who prepared Sr$_{1-x}$Mg$_x$TiO$_3$ thin films with Mg concentrations less than 0.3 mol% annealed at 750 and 900°C. Moreover, a marked shift towards higher wavenumber is observed in the position of the peaks as

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**Figure 3.** FTIR spectra of SrTiO$_3$ nanowire films doped with different Mg contents: a) uncalcined and b) calcined at 750°C for 2 h

**Figure 4.** Room temperature Raman spectra of SrTiO$_3$ nanowire films doped with different Mg contents: a) 0, b) 0.5, c) 1, d) 1.5 and e) 2 mol% calcined at 750°C for 2 h
the doping content increases, which can be attributed to the incorporation of Mg atoms at the Sr sites. However, according to the Raman results, degree of structural local-disorder due to the Mg doping in the SrTiO$_3$ lattice was confirmed. The appearance of some weak peaks, particularly at 281 and 439 cm$^{-1}$, can be the characteristic of MgO structure [29], which implies that the solubility of Mg in the SrTiO$_3$ nanowire films is restricted to less than 0.2 mol%, supporting the XRD and FTIR data.

FESEM/EDS images of the SrTiO$_3$ and SrTiO$_3$-1.5% Mg nanowire samples calcined at 750 °C for 2 h are shown in Fig. 5. As it can be seen, the nanowire arrays with a uniform diameter of ~100 nm were formed, although some fractured nanowires can also be seen. Figure 5b shows EDS microanalysis of the pure SrTiO$_3$ nanowires after calcination and removal of the alumina template by 0.1 M NaOH solution. It confirms that the nanowires contain essentially Sr, Ti and O elements, though a trace of Au is contained. The presence of Au peaks is attributed to the sputtering of the film surface. No peaks assigned to Al or other elements were detected in this spectrum, confirming that not only the AAO membrane but also fluoride and other impurities from the reactant were completely removed. FESEM image of the 1.5% Mg-doped SrTiO$_3$ nanowire film (Fig. 5c), indicates that the nanowires are smooth and close to each other. The average diameter of each nanowire is about 100 nm, which is in a good agreement with pore diameter of the AAO membrane. Some expansion and shrinkage can occur in diameter of the nanowires during the production process. It is explained that the shrinkage can be as a result of densification, water removal and residual materials from the as-prepared nanowires during the calcination process [30,31]. The widening of diameter can be due to chemical dissolution of the AAO membrane in the treatment solution during the nanowire formation in LPD process [32]. To understand the formation mechanism of the nanowires during LPD process, chemical reactions must be considered. In LPD process, hydroxide or metal oxide films can be formed by two hydrolysis reactions (ligand exchange reactions). Here, (NH$_4$)$_2$TiF$_6$ and Sr(NO$_3$)$_2$ were used as precursors, which dissociate to [TiF$_6$]$^{2-}$ and Sr$^{2+}$ ions in aque-
ous treatment solution. The expected hydrolysis reaction of $[\text{TiF}_6]^2-$ ion in aqueous solution is as follows [20,33,34]:

$$[\text{TiF}_6]^2- + n\text{H}_2\text{O} \rightleftharpoons [\text{TiF}_{6-n}(\text{OH})_n]^2- + n\text{H}^+ + n\text{F}^- \quad (2)$$

The sequence of reactions for the formation of SrTiO$_3$ films is as follows [8,30]:

$$\text{Sr}^{2+} + [\text{TiF}_{6-n}(\text{OH})_n]^2- \rightleftharpoons \text{Sr}[\text{TiF}_{6-n}(\text{OH})_n] \quad (3)$$
$$\text{Sr}^{2+} + \text{TiF}_6^2- \rightarrow \text{Sr}[\text{TiF}_6] \quad (4)$$
$$\text{Sr}[\text{TiF}_6] + n\text{H}_2\text{O} \rightleftharpoons \text{Sr}[\text{TiF}_{6-n}(\text{OH})_n] + n\text{H}^+ + n\text{F}^- \quad (5)$$

However, ligand-exchange equilibrium reaction 2 or 5 can be shifted to the right side if alumina membrane is used. Then, the F$^-$ ions consuming reaction takes place to form a stable complex. In fact, AAO membranes are dissolved according to the reaction 6, which provides scavengers for fluoride ions [32]:

$$\text{Al}_2\text{O}_3 + 12\text{H}^+ + 12\text{F}^- \rightarrow 2\text{H}_3\text{AlF}_6 + 3\text{H}_2\text{O} \quad (6)$$

At the beginning, Sr[\text{TiF}_{6-n}(\text{OH})_n] is expected to be deposited on the surface and then extended into the inner part of AAO membrane with prolonging reaction time. The dehydration reactions of Sr[\text{TiF}_{6-n}(\text{OH})_n] precursor solid into SrTiO$_3$ can occur during calcination at $>500^\circ\text{C}$ [8]:

$$\text{Sr}[\text{TiF}_{6-n}(\text{OH})_n] \rightarrow \text{SrTiO}_3 + (n-3)\text{H}_2\text{O} + (6-n)\text{HF} \quad (7)$$

For the 1.5% Mg-doped SrTiO$_3$ sample, EDS spectrum shown in Fig. 5d exhibits a small but clear Mg peak along with Sr, Ti, O and Au ones, confirming incorporation of Mg into the SrTiO$_3$ lattice. This result is in a good agreement with the XRD pattern. No additional peaks appeared in EDS spectrum, thereby suggesting complete removal of the alumina template and other residual impurities from the nanowire film.

Dielectric behaviour of the Mg-doped SrTiO$_3$ nanowire films calcined at 750$^\circ\text{C}$ for 2 h is presented in Fig. 6. It can be observed that the dielectric constant decreases obviously as the frequency increases (Fig. 6a), demonstrating that the polarization spinning cannot catch up with the frequency of the electric field [35]. In the low-frequency region, the electrical change easily causes a dipolar moment, resulting in the increase of $\varepsilon_r$ value [36]. Dielectric constant of the samples experimentally increases from $\varepsilon_r = 393.8$ to 594.2 (at 1 kHz) by increasing Mg content in the SrTiO$_3$ nanowire films. The improvement of $\varepsilon_r$ value may be due to the increased average ionic polarization in the compositions. Notably, dielectric constant of the 1.5% Mg-doped SrTiO$_3$ sample is considerably higher compared to the pure SrTiO$_3$ sample (approximately 1.5 times at 1 kHz). The high dielectric constant of the nanowire films exhibits high polarization under the applied electric field, thus it can be advantageous for improving energy storage density in the dielectric materials. At high frequency beyond the relaxation one, there are no changes of dielectric constant and it is almost independent of frequency. In this region, charge carriers do not have enough time for long-range hopping before field reversal [36].

Figure 6b shows frequency-dependent dielectric loss of the pure SrTiO$_3$ and Mg-doped SrTiO$_3$ nanowire films. As shown, all the samples indicate a decreased tendency of the dielectric loss-frequency characteristics. Dielectric loss of a material with relaxation polarization and conductivity depends on the applied field frequency in a complicated manner. In the high-frequency region from 10 kHz to 1 MHz, dielectric loss remains almost constant because the electron exchange interaction cannot follow the alternation of the applied electric field beyond the relaxation frequency. Meanwhile, Mg incorporation causes a gradual reduction in dielectric loss values. Specifically, the 1.5% Mg-doped SrTiO$_3$ nanowire films have minimum dielectric loss value equal to 0.0119 at 100 kHz. The low dielectric loss of this sample confirms good dielectric quality of the prepared material, showing low energy loss [9]. The minimum $\varepsilon_r$ and maximum $\tan \delta$ were obtained for the 2.0% Mg-doped SrTiO$_3$ sample, which may be due to the presence of secondary MgO phase. It is well

Figure 6. Variation of dielectric constant (a) and dielectric loss (b) of the pure SrTiO$_3$ and Mg-doped SrTiO$_3$ nanowire films as a function of frequency
known that dielectric loss is strongly affected by the microstructural factors like grain size, crystallinity, porosity, lattice defects and secondary phases [37,38].

Dielectric breakdown strength ($E_b$) is another important factor to evaluate the performance of dielectric devices. The dielectric breakdown strength of materials is ascribed as the maximum electric potential that dielectric material can resist without losing its insulating properties [39]. Thus, characteristic breakdown strength of the pure SrTiO$_3$ and Mg-doped SrTiO$_3$ nanowire films was further evaluated by two parameter Weibull distribution. The mathematical framework for the Weibull distribution can be described by the following equations [1]:

$$X_i = \ln (E_i)$$  \hspace{1cm} (8)

$$Y_i = \ln \left( -\ln \left( 1 - \frac{i}{n+1} \right) \right)$$ \hspace{1cm} (9)

where, $E_i$ is measured breakdown field of each specimen in the experiment, $i$ is serial number of nanowire films arranged in ascending order of $E_b$ values and $n$ is sum of the specimens of each composition. $X_i$ and $Y_i$ are two indicators in the Weibull distribution that have a linear relationship together, demonstrating that all data points were well fitted with the Weibull distribution, as shown in Fig. 7a. The average breakdown strength can be obtained from the fitted lines intersecting with the horizontal axis through $Y_i = 0$. The slope of these fitted lines is called the shape parameter ($\beta$) that evaluates the scattering state of the data so that a greater $\beta$ presents better reliability. It can be seen that $E_b$ of SrTiO$_3$ nanowire films with 0.5, 1 and 1.5 mol% Mg are 368.7, 395.4 and 463.1 kV/cm, respectively, which is higher than that of the pure SrTiO$_3$ nanowire film (287.1 kV/cm). Incorporation of Mg into the SrTiO$_3$ lattice effectively improves $E_b$ of the nanowire films, and the highest $E_b$ value is attributed to 1.5 mol% Mg. However, this high breakdown strength can be related to various parameters, including porosity, electrode configuration, grain size, thickness, defects and secondary phase [9]. With further increase in Mg content to 2 mol%, $E_b$ declines (428.4 kV/cm), which can be related to the presence of MgO as a secondary phase in the composition. Furthermore, the Weibull coefficient, $\beta$, for the pure SrTiO$_3$ and 0.5, 1.0, 1.5 and 2.0 mol% Mg-doped SrTiO$_3$ nanowire films was estimated to be 4.05, 5.01, 6.44, 7.88 and 4.46, respectively. It can be observed that $\beta$ values slightly increase by increasing Mg content up to 1.5 mol%, and then decrease. As $\beta$ quantifies the scattering in the experimental data; increased $\beta$ indicates less scattering. However, according to the aforementioned dielectric behaviour, it seems reasonable that the Mg-doped SrTiO$_3$ nanowire films can possess high dielectric constants and low dielectric loss combined with relatively high $E_b$ and $\beta$ values, which make them suitable candidates for energy storage devices.

Moreover, the maximum volumetric energy density ($U_{max}$) of the nanowire films is directly related to dielectric breakdown strength ($E_b$) and relative dielectric constant ($\varepsilon_r$) according to the classical equation [39]:

$$U_{max} = \frac{\varepsilon_r \cdot \varepsilon_0 \cdot E_b^2}{2}$$ \hspace{1cm} (10)

Figure 7b presents $U_{max}$ of the pure and SrTiO$_3$ nanowire films doped with different Mg contents. It is found that the energy density at first enhances from 1.44 to 5.64 J/cm$^3$ by increasing Mg content from 0 to 1.5 mol% and then decreases to 3.13 J/cm$^3$ when Mg content reaches 2 mol%. Therefore, high dielectric constant accompanied by high dielectric breakdown strength in the 1.5% Mg-doped SrTiO$_3$ sample results in the highest energy density, suggesting that nanowire film can be a promising material to fabricate high voltage capacitors with high energy-storage density.

IV. Conclusions

In this research, we reported a systematic study of structure and dielectric properties of the SrTiO$_3$ nanowire films with different Mg doping contents (from 0 to 2 mol%) prepared by LPD process. FESEM studies
revealed that the aligned nanowire films with an average diameter of about 100 nm were formed, which are comparable to dimensions of the AAO membrane template pores. It was found that dielectric constant and breakdown strength at first increased by increasing Mg content and then decreased. The optimal composition was obtained at 1.5 mol% Mg, demonstrating the highest dielectric constant (594.2), low dielectric loss (0.0167) and the highest breakdown strength (463.1 kV/cm) at 1 kHz. Moreover, this nanowire film also exhibited an enhanced energy density of 5.64 J/cm³, which is about 3.9 times higher than that of the pure SrTiO₃ nanowire films (1.44 J/cm³). Based on the aforementioned results, the Mg-doped SrTiO₃ nanowire films can be potential candidates for high energy-density dielectric capacitor applications.

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