Preparation of Micro-Patterned CaMn$_7$O$_{12}$ Ceramic Films via a Photosensitive Sol-Gel Method

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Received: 24 August 2019; Accepted: 8 October 2019; Published: 9 October 2019

Abstract: Mn/acetylacetone chelate was synthesized using Mn(CH$_3$COO)$_2$·4H$_2$O as raw material, methanol as the solvent, and acetylacetone as the chelating agent. The ultraviolet (UV)-absorption peak of the synthesized chelate was found around 298 nm. CaMn$_7$O$_{12}$ sol was subsequently prepared using the Mn/AcAc chelate as the Mn source and calcium nitrate as the calcium source. The UV test indicates that the CaMn$_7$O$_{12}$ sol has the UV-sensitive characteristics. Owing to its photo-sensitivity, micro-patterned CaMn$_7$O$_{12}$ ceramic film can be prepared without photoresist, only through dip-coating, drying, UV-irradiation, solvent-washing, and heat treatment. The magnetic test result indicates that the micro-patterned CaMn$_7$O$_{12}$ ceramic film has a saturation magnetization of 112.8 emu/cm$^3$, which is close to that of non-patterned CaMn$_7$O$_{12}$ ceramic film.

Keywords: CaMn$_7$O$_{12}$; multiferroic film; micro-pattern; sol-gel

1. Introduction

A multiferroic material refers to a material that simultaneously has a ferroic order of two or more, such as ferroelectric (reverse), ferromagnetic (reverse), or ferroelastic sequences [1–5]. As the second type of single-phase multiferroic material, CaMn$_7$O$_{12}$ has ferroelectric properties caused by its special helical magnetic structure, and produces a strong magneto-electric coupling effect. Therefore, CaMn$_7$O$_{12}$ has potential applications in spin electronics, multi-state storage devices, and microelectromechanical system (MEMS) [6–12]. In recent years, while there have been more studies on the structure and performance of bulk CaMn$_7$O$_{12}$ (including single crystals and polycrystalline samples), there have been few studies on CaMn$_7$O$_{12}$ film [13–18]. In 2015, Huon et al. deposited c-axis oriented CaMn$_7$O$_{12}$ film. Subsequently, they studied the helical magnetic ordering structure of the Sr-doped CaMn$_7$O$_{12}$ film [19–21]. In 2018, our group adopted sol-gel technology to prepare a CaMn$_7$O$_{12}$ ceramic film with good bi-axial texture on a LaAlO$_3$ (LAO) substrate; the work confirmed that the saturation magnetization of the CaMn$_7$O$_{12}$ ceramic film was better than that of the bulk material [22].

Micro-patternning is required when applying single-phase multiferroic CaMn$_7$O$_{12}$ to the microelectronics field. The traditional photoresist etching process includes preparing film, coating photoresist, ultraviolet (UV) exposure, leaching, photoresist removal, etc. [23]. However, it has a few disadvantages such as requiring expensive processing equipment, the complex process, time-consuming, and ion damage. Furthermore, expensive photoresist is essential for transferring a geometric pattern structure from a mask to films [24,25]. UV-photosensitive sol-gel technology is a new technology that can be applied to the micro-fabrication for film. In the preparation of sols some chemical modifier was added in the sol precursor, and it can coordinate with some metal ions to form chelating structures.
Under the UV irradiation, these structures decompose rapidly resulting in changes the solubility of its gel film in organic solvent. Making use of the different solubility, the micro-pattern consistent with the negative phase of mask can be prepared. As a result, the photosensitive sol-gel method shows many advantages such as large deposition area, simple process, and low process as well [26].

In our previous work, the method was successfully applied for the preparation of micro-patterns on various functional films, such as on ZnO, BiFeO₃, YBa₂Cu₃O₇−ₓ, WO₃, ZrO−SiO₂, and La₀.₆₇Sr₀.₃₃MnO₃ [26–31]. In this paper, the UV-photosensitive sol-gel technology was further applied to the preparation of micro-patterned CaMn₇O₁₂ ceramic film. Micro-patterned CaMn₇O₁₂ ceramic film with a clear profile and a regular structure was facilely obtained. In addition, the magnetic properties of micro-patterned CaMn₇O₁₂ ceramic film was characterized with vibrating-sample magnetometer (VSM) and compared with that of the un-patterned one.

2. Experimental

2.1. Preparation of Photosensitive CaMn₇O₁₂ Sol

The CaMn₇O₁₂ sol was prepared with a metal ion ratio of Ca:Mn = 1:7 in the sol. Ca(NO₃)₂·4H₂O and Mn(CH₃COO)₂·4H₂O were used as raw materials, methanol (MeOH) was used as the solvent, and acetylacetone (AcAc) was used as the chelating agent. First, 0.1771 g of Ca(NO₃)₂·4H₂O (0.75 mmol) was dissolved in 5 mL of anhydrous MeOH to obtain solution A; then, 1.2867 g (5.2 mmol) of Mn(CH₃COO)₂·4H₂O was added to 5 mL of anhydrous MeOH and 0.53 g of AcAc as the chelating agent (5.2 mmol) was further added. After stirring, the mixture became clear and was named solution B. Solutions A and B were mixed and stirred and the total metal ion concentration was adjusted to 0.4 mol/L by changing the amount of MeOH and allowed to stand for 24 h to obtain a stable and uniform CaMn₇O₁₂ UV-photosensitive sol.

2.2. Preparation of Micro-Patterned CaMn₇O₁₂ Ceramic Film

Using LaAlO₃ as a substrate, the CaMn₇O₁₂ gel film was obtained via dip-coating in a glove box with a humidity <30% R.H. The pulling speed was 2 mm/s and the temperature was 25 °C. The thickness of the obtained CaMn₇O₁₂ gel film was 207 nm. The gel film was dried at 80 °C for 10 min, then irradiated in air for 60 min through a mask. Then, the film was washed in a mixed solution of ethanol and n-butanol (molar ratio 10:1) for 15 s to obtain the patterned CaMn₇O₁₂ gel film. After that the patterned CaMn₇O₁₂ gel film was dried at 350 °C in a heat treatment furnace for 10 min to remove the organic components. Finally, the film was heat treated at 730 °C for 60 min to obtain a crystallized CaMn₇O₁₂ ceramic film with a pattern structure. Its thickness was 49 nm. The specific preparation process is also shown in Figure 1.

![Figure 1. Preparation flowchart of the micro-patterned CaMn₇O₁₂ ceramic film.](image)

2.3. Characterizations

Phase and orientation of micro-patterned CaMn₇O₁₂ ceramic film with striped structure were analyzed by X-ray diffractometer (XRD) with Cu Kα radiation (7000S, Shimadzu, Kyoto, Japan). The absorption spectrum and photosensitive performance of the as-prepared sol and its gel film
were recorded with an Ultraviolet-visible spectrometer (UV-Vis) (V-570, Shimadzu, Kyoto, Japan). Thickness of films was executed by VASE Ellipsometer (VB-400, J.A.Woollam, Lincoln, NE, USA). The chemical composition of the ceramic film was determined by energy dispersive X-ray spectrometry (EDS). An optical microscope (Olympus, BX51, Tokyo, Japan), a laser confocal scanning microscopy (LCSM) (Olympus OLS4000, Tokyo, Japan), and a scanning electron microscope (SEM) (JSM-7000F, JOEL, Tokyo, Japan) were used to observe the surface morphology of the micro-patterned CaMn$_7$O$_{12}$ ceramic films. The UV exposure process was carried out using the UV light source (USHIO SP-9, Tokyo, Japan), which was a high-pressure mercury lamp (UXM-Q256BY) with a power of 250 W and a main wavelength range from 220 to 375 nm. The distance between the sample and the lamp was 10 cm, and the as-obtained light intensity was 97 mW/cm$^2$. Saturation magnetization and coercivity were performed with a multi-function vibrating sample magnetometer (VSM) in a physical property measurement system (VersaLab, Quantum Design, San Diego, CA, USA).

3. Results and Discussion

3.1. Photo-Sensitivity of the CaMn$_7$O$_{12}$ Sol and Its Gel Thin Film

To study the photo-sensitivity of the CaMn$_7$O$_{12}$ sol and its gel film, the UV spectra of the AcAc and MeOH (AcAc + MeOH) mixture, a solution containing Ca$^{2+}$ (Ca + AcAc + MeOH), a solution containing Mn$^{2+}$ (Mn + AcAc + MeOH), and a CaMn$_7$O$_{12}$ sol were measured and the results are shown in Figure 2. It can be seen that the characteristic UV absorption peak of AcAc-MeOH solution is at 274 nm and the peak is attributed to the $\pi-\pi^{*}$ electron transition of the K-adsorption band of the enol structure of AcAc. After adding a Ca$^{2+}$ into the solution, the characteristic UV adsorption peak was still at 274 nm, indicating that the enol structure of AcAc was still present and Ca$^{2+}$ does not react with AcAc. After adding the manganese ion into the solution, the characteristic UV adsorption peak occurs at 298 nm. Compared with the adsorption peak of the enol structure of AcAc, there was a red-shift of 24 nm, indicating a chelating reaction between Mn(CH$_3$COO)$_2$$ \cdot$4H$_2$O and AcAc. In the reaction between Mn$^{2+}$ and AcAc, the acetic group was partially substituted by AcAc through chemical coordination, as shown in Scheme 1. The red-shift of the characteristic UV absorption peak is ascribed to the above reaction. Therefore, the absorption peak at 298 nm corresponds to the $\pi-\pi^{*}$ transition of the Mn/AcAc metal-coordinated chelate rings formed between Mn$^{2+}$ and AcAc [32].

![Figure 2. Ultraviolet-visible spectrometer (UV-Vis) spectra of CaMn$_7$O$_{12}$ gel in different stages: (a) AcAc + MeOH, (b) Ca + AcAc + MeOH, (c) Mn + AcAc + MeOH and (d) CaMn$_7$O$_{12}$ sol.](image-url)
Scheme 1. Chelating reaction between Mn(CH$_3$COO)$_2$·4H$_2$O and AcAc.

The UV absorption spectrum of the CaMn$_7$O$_{12}$ precursor sol is also shown in Figure 2. The main characteristic absorption peak at 298 nm is consistent with the absorption peak of Mn/AcAc chelate, which means that the addition of Ca$^{2+}$ does not cause the destruction of the structure of Mn/AcAc chelate, and the UV absorption of the CaMn$_7$O$_{12}$ sol is derived from the Mn/AcAc chelate.

The CaMn$_7$O$_{12}$ gel film was obtained via the dip-coating method, the variation in the UV spectrum of the CaMn$_7$O$_{12}$ gel film with irradiation time was tested and is shown in Figure 3. The UV absorption spectra of CaMn$_7$O$_{12}$ gel film around 330 nm became wider compared with that of CaMn$_7$O$_{12}$ sol, which was related to the different states of chelate molecules in the sol and gel film. In the sol, the chelate molecules exist in a free form. While in the gel film, the chelate molecules exist in a stacked form, then causing intermolecular electron transfer. The migration of electrons leads to the variation of energy levels and band, resulting in the wideness of the UV absorption spectrum of the CaMn$_7$O$_{12}$ gel film [33,34]. As the irradiation time is prolonged, the characteristic absorption peak that characterizes the chelate content gradually became smaller, indicating that the corresponding coordinated chelate in the gel film was continuously photo-decomposed and the concentration of the coordinated chelate decreases. The reason is that under the irradiation condition of UV lamp, the chelates in CaMn$_7$O$_{12}$ gel film absorbs UV irradiation with a certain wavelength ($\lambda > 200$ nm) and then electron excitation occurs (Scheme 2). As the excited state is unstable, further reactions can take place (Scheme 3). Since a portion of electrons distributes around the oxygen atoms, the electrons excitation can reduce the coordination intensity of AcAc. Therefore, the chelating structures break continuously as the irradiation time prolongs [26]. This chemical structural change of the gel film can significantly change its solubility in organic solvents. Making use of the photo-sensitive characteristics, the gel film was irradiated by UV light through a mask and then washed in organic solvent. During the process, the regions shielded by the mask can be washed away and the regions exposed to the UV light remain intact, resulting in a fine pattern consistent with the negative image of the mask.

Figure 3. UV-Vis absorption spectra of the CaMn$_7$O$_{12}$ gel film at different UV irradiation times.
Scheme 2. Expression of electron excitation process.

Scheme 3. Decomposition process of excited state.

3.2. Phase Composition of Micro-Patterned CaMn₇O₁₂ Ceramic Film

In order to further ascertain crystallization process of the micro-patterned CaMn₇O₁₂ ceramic film, CaMn₇O₁₂ films sintered at different temperatures ranging from 600 to 750 °C were characterized by XRD measurement. As shown in Figure 4, the CaMn₇O₁₂ film sintered below 700 °C was incomplete crystallized, because only a weak diffraction peak (2θ = 49.38°) of CaMn₇O₁₂ (002) was observed. When the sintering temperature was heated up to 730 °C, another reflection peak at 2θ = 24.09° corresponding to (001) CaMn₇O₁₂ phase appeared and no intermediate phase was detected (according to the JCPDF standards, Card No. 26-1114) [19]. In addition, as sintered temperature was raised to 75 °C, diffraction peaks intensity of CaMn₇O₁₂ phase had no significant increase. It indicated that the crystallization of CaMn₇O₁₂ phase in the CaMn₇O₁₂ film had completed at ~730 °C. From the point of view of energy and environmental protection, 730 °C was chosen as the optimum sintered temperature. Compared with LaAlO₃ substrate, the diffraction peaks of CaMn₇O₁₂ ceramic films were weaker because of their smaller thickness.

Figure 4. X-ray diffractometer (XRD) pattern of CaMn₇O₁₂ ceramic films sintered at different temperatures.
3.3. Micrograph of Micro-Patterned CaMn$_7$O$_{12}$ Ceramic Film

Micro-patterned CaMn$_7$O$_{12}$ ceramic films were prepared with masks having stripe, dot-matrix, and radial structures respectively. Figure 5a shows an optical micrograph of the film with strip structure, where the lighter regions are LaAlO$_3$ matrix while the darker regions are CaMn$_7$O$_{12}$ ceramic film. It can be seen that the pattern on CaMn$_7$O$_{12}$ ceramic film has a clear profile and a uniform surface. Figure 5b shows SEM photograph of yellow selected area in Figure 5a. It can be seen that the film is compact and crack-free, and the grain size is uniform. The average particle size is about 180 nm, which is close to the particle size of the pristine CaMn$_7$O$_{12}$ ceramic film prepared in the previous study [22]. Figure 5c shows the laser confocal graphs of the film with dot-matrix (the inset is its 3D graph). The diameter and period of columns in dot-matrix structure are both 50 µm. The pattern is also clear and regular, without cracks or pores. Figure 5d shows the laser confocal graph of the film with radial structure, indicating the minimum line width in the micro-fabrication process can reach 5 µm.

![Figure 5a](image)

(a) Optical micrograph of film with strip structure.

![Figure 5b](image)

(b) SEM photograph of yellow selected area in Figure 5a.

![Figure 5c](image)

(c) Laser confocal graphs of film with dot-matrix structure.

![Figure 5d](image)

(d) Laser confocal graph of film with radial structure.

**Figure 5.** Micrographs of micro-patterned CaMn$_7$O$_{12}$ ceramic films: (a) optical micrograph of the film with strip structure; (b) scanning electron microscope (SEM) photograph of yellow selected area in (a); (c) laser confocal graphs of the film with dot-matrix (the inset is its 3D graph), and (d) laser confocal graph of the film with radial structure.

3.4. Magnetic Properties of the Micro-Patterned CaMn$_7$O$_{12}$ Ceramic Film

The magnetic property of micro-patterned CaMn$_7$O$_{12}$ ceramic film with dot-matrix structure is shown in Figure 6. It can be seen that the micro-patterned CaMn$_7$O$_{12}$ ceramic film exhibits apparent anti-ferromagnetic characteristics. The properties include a saturation magnetization ($M_s$) of 112.8 emu/cm$^3$ and a coercivity ($H_c$) of 211 Oe, which are close to the saturation magnetization ($M_s = 114.2$ emu/cm$^3$, $H_c = 220$ Oe) of the CaMn$_7$O$_{12}$ ceramic film without patterned structure [22]. The result indicates that the photosensitive sol-gel micro-patterning process does not affect the magnetic properties of the CaMn$_7$O$_{12}$ film. The magnetic properties of multiferroic films are generally affected by factors such as grain size, grain morphology, grain boundaries, etc. However, for the process
of preparing fine patterns by the photosensitive sol-gel method, the micro-patterning process was performed prior to annealing treatment. Consequently, the crystallinity of the film was not affected. As a result, the magnetic properties of pattern ceramic films would not have been affected significantly [30].

Figure 6. Magnetic hysteresis loop of the micro-patterned CaMn\textsubscript{7}O\textsubscript{12} ceramic film at 50 K. The inset depicts the partial enlarged view of the M-H loop at near zero magnetic field.

4. Conclusions

In the paper, a CaMn\textsubscript{7}O\textsubscript{12} sol with UV sensitivity was prepared using Ca(NO\textsubscript{3}\textsubscript{2})\textsubscript{2}-4H\textsubscript{2}O and Mn(CH\textsubscript{3}COO)\textsubscript{2}
\textsubscript{4H\textsubscript{2}O as the raw materials, MeOH as a solvent, and AcAc as a chemical modifier. The Mn\textsuperscript{2+} in sol can chelate with AcAc, then form an Mn/AcAc metal-coordinated chelate ring, resulting in an obvious UV-absorption peak at 298 nm. CaMn\textsubscript{7}O\textsubscript{12} gel film was obtained through dip-coating process. After processes including masking, UV-radiation, solvent washing, the micro-patterned CaMn\textsubscript{7}O\textsubscript{12} gel film was obtained. After heat treatment at 730 °C, the micro-patterned CaMn\textsubscript{7}O\textsubscript{12} gel film was converted into the micro-patterned crystalline CaMn\textsubscript{7}O\textsubscript{12} ceramic film. The saturation magnetization at 50 K of the micro-patterned CaMn\textsubscript{7}O\textsubscript{12} ceramic film reached 112.8 emu/cm\textsuperscript{3}, which was close to the performance of the ceramic film without micro-fabrication.

**Author Contributions:** Designed the research project, G.Z.; performed all experiments, Y.W. and C.W.; characterized samples and analyzed corresponding data, Y.W. and C.W.; wrote the initial draft and provided valuable comments and suggestions to the work, Z.D.

**Funding:** This work was supported by the project of the National Natural Science Foundation of China (51672212), the Scientific Research Fund (2013J0676) of the Department of Education and Nature Science Foundation (2018M5019) of Shaanxi Province, the Fund Project (16ZB0470) of Sichuan Provincial Department of Education, the Invested by the Seed Capital of Panzhihua University Science and Technology Park (2019-12), the Doctoral Fund (bkqj2017009) and Student Innovation and Entrepreneurship Training Project (2019ccxy059) of Panzhihua University.

**Conflicts of Interest:** The authors declare no conflict of interest.

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