

# One step preparation of photosensitive $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$ films and their fine patterns by a photosensitive sol–gel method

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## Abstract

An acrylic acid-modified photosensitive sol–gel method is proposed to prepare  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$  (Bi-2212) gel films and their fine patterns on  $\text{LaAlO}_3$  (LAO) single crystal substrates. An ultraviolet–visible absorption spectrum showed the UV characteristic absorption peak at around 270 ~ 280 nm which originates from the  $\pi$ - $\pi^*$  electron transition of acrylic acid in metal complexes, and its intensity decreases as the UV irradiation time increases, indicating that Bi-2212 gel films are photosensitive. Based on the photosensitivity of Bi-2212 gel films, fine-patterned Bi-2212 gel films with the smallest resolution of 3  $\mu\text{m}$  have been prepared. The prepared fine-patterned Bi-2212 superconducting films exhibit *c*-axis growth orientation and excellent superconducting properties.

Keywords: Bi-2212 films, photosensitive sol–gel, fine patterns, superconductivity

(Some figures may appear in colour only in the online journal)

## 1. Introduction

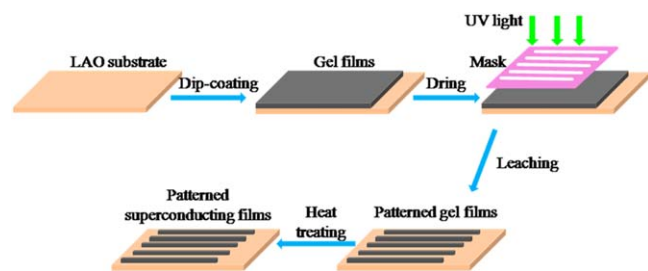
Since the discovery of Bi-based superconductors, Bi-2212 has attracted considerable attention, due to its unique physical and structural characteristics such as a high anisotropic and two-dimensionality, a short coherence length, and intrinsic Josephson effects, without rare earth elements or toxic elements. Bi-2212 high- $T_c$  superconducting films can be widely applied in superconducting microelectronic fields on the condition that they often need to be fine-patterned [1–5]. In recent years, much effort has been put into the development of the fine-patterning technology of films by our research group, and a photosensitive sol–gel method has progressed. This method provides a new fine-patterning method for the high- $T_c$  superconducting films that are applied in superconducting microelectronic devices [6–8]. Compared with some traditional fine-patterning methods such as wet chemical etching [9], focused ion beam [10, 11], laser patterning [12, 13], and high energy ion irradiation [14], the

photosensitive sol–gel method dramatically reduces surface damage and property degradation resulting from ion beam or etching agent, and realizes the integration and high-efficiency of a microstructure.

The photosensitive sol–gel method combines a chemical modification method and the sol–gel method. The solutions modified by chemical modifiers will be photosensitive. When gel films are irradiated in air with UV light, it results in a change of solubility in organic solvent, then their fine patterns can be prepared after leaching in an organic solvent.

In this paper, an acrylic acid (AA)-modified photosensitive sol–gel method for Bi-2212 photosensitive sol and their fine patterns has been proposed. The main purpose of this research paper is to use AA either as a chemical modifier or as photosensitive modifier to prepare photosensitive Bi-2212 sol, and study the formation possibility and photosensitivity of the metal complexes formed by metal ions and AA. It is found that using the photosensitivity of Bi-2212 films, the simultaneous preparation of Bi-2212 gel films and their fine patterns can be realized. After heat treating the fine-patterned Bi-2212 gel films, fine-patterned Bi-2212 superconducting films can be prepared.

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**Figure 1.** Schematic diagram of the fine-patterned procedure of Bi-2212 films.

## 2. Experiment

### 2.1. Preparation of photosensitive Bi-2212 solution

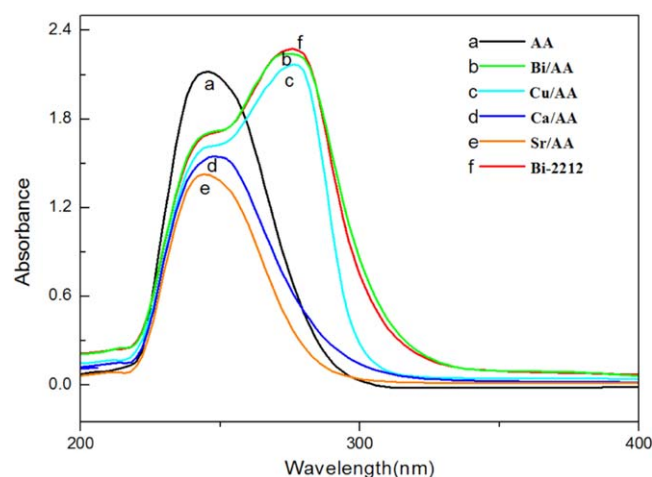
Analytical reagents  $\text{Bi}(\text{CH}_3\text{COO})_3 \cdot \text{Bi}(\text{OAc})_3$ ,  $\text{Sr}(\text{CH}_3\text{COO})_2 \cdot 1/2\text{H}_2\text{O}$  ( $\text{Sr}(\text{OAc})_2$ ),  $\text{Ca}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$  ( $\text{Ca}(\text{OAc})_2$ ), and  $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$  ( $\text{Cu}(\text{OAc})_2$ ) were used as starting materials, AA and methanol were used as the chemical modifier and solvent to synthesize the Bi/AA solution, Sr/AA solution, Ca/AA solution, and Cu/AA solution, respectively. Then, with the molar ratio of metallic ions controlled at Bi:Sr:Ca:Cu:AA = 2:2:1:2:40, mixing of the four solutions was done to obtain blue photosensitive Bi-2212 sol. Bi-2212 gel films were fabricated on quartz and silicon substrates by the dip-coating technique so as to measure their ultraviolet–visible (UV–vis) absorption spectra and Fourier transform infrared (FT-IR) spectra. And their fine patterns were prepared on LAO single crystal substrates by the photosensitive sol–gel method. Details of the preparation process of the Bi-2212 sol and the heat treatment process of the Bi-2212 superconducting thin films have been illustrated in [15].

### 2.2. Fine patterns of Bi-2212 gel film

Figure 1 shows the fine-patterning process of Bi-2212 gel films. Photosensitive Bi-2212 gel films were dip-coated on LAO substrates, and dried at 80 °C for 1–2 min. Subsequently, the photosensitive Bi-2212 gel films were irradiated for 40 min by a high pressure Hg vapor lamp through a mask with a specific shape, and then leached in a mixture solution of methanol and isopropyl alcohol at a mole ratio of 8:2 for 40–100 s. After leaching, the unirradiated area of the gel films dissolved, while the irradiated area remained in its original state. As a result, Bi-2212 gel films with the desired fine patterns were obtained. Finally, fine-patterned Bi-2212 superconducting films were prepared after subjecting the fine-patterned Bi-2212 gel films to an appropriate heat treatment process. Details of the preparation process of Bi-2212 gel films after photo-fabrication have been described elsewhere [15].

### 2.3. Characterization

UV exposure experiments were carried out using a UV spot lamp ( $250 \text{ mW cm}^{-2}$ , SP-7-250DB) at room temperature. FT-IR spectra of the photosensitive Bi-2212 gel films coated on the silicon wafer were measured with a FT-IR



**Figure 2.** UV–vis absorption spectra for different solutions.

spectrophotometer (IR Prestige-21). The optical absorption spectra of the Bi-2212 gel films coated on quartz glass substrates were measured using a UV–vis spectrometer (TU-1901). The phases and crystal orientation of the Bi-2212 films were detected by an x-ray diffractometer (XRD-7000S). Curves depicting the resistance–temperature ( $R$ – $T$ ) characteristics and magnetic hysteresis loop of the films were measured by A Versa Lab multi-function vibrating sample magnetometer.

## 3. Results and discussion

Summarizing the chemical reactions occurred in the photosensitive Bi-2212 sol. Acrylic acid can react with metal ions ( $\text{Bi}^{3+}$ ,  $\text{Cu}^{2+}$ ) in the solution to form metal complexes which can absorb UV–vis light. After a certain amount of time under UV irradiation, the metal complexes are photolyzed and they are insoluble in leaching solvent that contains methanol and isopropyl alcohol, while the unirradiated region in the Bi-2212 gel films can be dissolved in organic solvent, the irradiated region finally remained.

### 3.1. Photosensitivity of Bi-2212 sol and its gel films

Figure 2 shows the UV–vis absorption spectra of different solutions. The UV–vis absorption spectrum of AA dissolving in methanol (AA) with a characteristic absorption peak at around 246 nm which originates from the  $\pi$ – $\pi^*$  electron transition of AA, is shown in figure 2(a) [16].

Figures 2(b)–(e) show the UV characteristic absorption spectra of the Bi/AA solution, Cu/AA solution, Ca/AA solution, and Sr/AA solution, and the characteristic absorption peak at 270 ~ 280 nm was observed in the UV characteristic absorption spectra of the Bi/AA solution and the Cu/AA solution, while not observed in those of the Ca/AA solution and the Sr/AA solution. The appearance of an absorption peak at 270 ~ 280 nm indicates that some chemical reactions, which change the  $\pi$ – $\pi^*$  electron transition of AA, occur in the Bi/AA solution and Cu/AA solution.

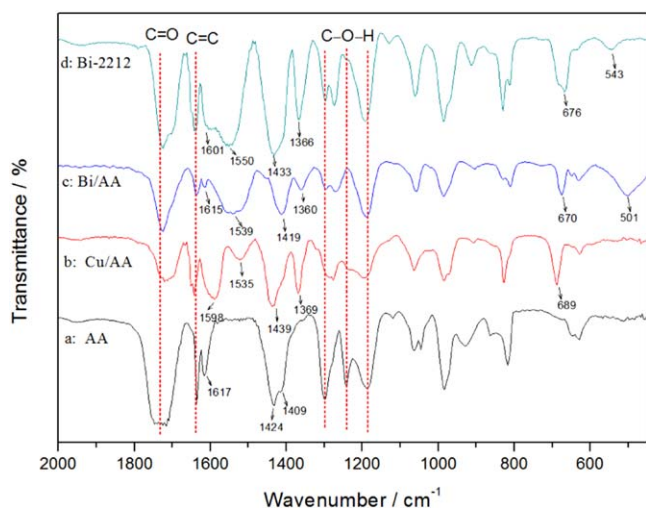


Figure 3. IR spectra of several gel films.

Figure 2(f) shows the UV characteristic absorption spectrum of the Bi-2212-sol. An absorption peak at 270 ~ 280 nm was also observed, which originates from the  $\pi$ - $\pi^*$  transition of metal complexes, indicating that metal complexes formed by AA reacting with  $\text{Bi}(\text{OAc})_3$  and  $\text{Cu}(\text{OAc})_2$  could stably exist in the Bi-2212 sol.

In order to further investigate the photosensitivity of Bi-2212 gel films, FT-IR spectra measurements are performed on AA, Bi/AA, Cu/AA, and Bi-2212 gel films, as shown in figure 3. As can be seen, the characteristic peak of C=O stretching vibration absorption at  $1729\text{ cm}^{-1}$  was observed in the FT-IR spectrum of AA (figure 3(a)), and the non-isomorphic stretching vibrations of the C=C bond appear at  $1636\text{ cm}^{-1}$  and  $1617\text{ cm}^{-1}$ .

Figure 3(b) shows the FT-IR spectrum of the Cu/AA gel films, where C=O stretching vibration appears at lower wave numbers ( $1719\text{ cm}^{-1}$ ) and C=C stretching vibration appears at higher wave numbers ( $1642\text{ cm}^{-1}$ ) compared with that of AA dissolving in methanol. The FT-IR spectrum also has  $\nu_a(\text{COO}^-)$  at  $1598\text{ cm}^{-1}$  and  $1535\text{ cm}^{-1}$  and  $\nu_s(\text{COO}^-)$  at  $1439\text{ cm}^{-1}$  and  $1369\text{ cm}^{-1}$  [17, 18], and the characteristic peak at  $689\text{ cm}^{-1}$  is assigned to the Cu-O stretching vibration of the Cu complex [19]. The above results indicate that the coordination reaction happened between the AA and the Cu ion rather than an ionic reaction. The FT-IR spectra of the Cu/AA gel films show the difference between  $\nu_a(\text{COO}^-)$  and  $\nu_s(\text{COO}^-)$  is about  $160\text{ cm}^{-1}$ , and it demonstrates that two symmetry dependant neighbors in the chain are connected by a strong O-H...O hydrogen bridge [20]. Based on the FT-IR analysis, a schematic structure of the Cu complex is illustrated in figure 4. During the reaction of Cu ion with AA, the hydroxyl oxygen atom of AA provides a lone pair electrons to the Cu ion, which causes the characteristic peaks of C=O and C=C of AA to shift to a lower wave number and higher wave number, respectively.

Figure 3(c) shows FT-IR spectrum of the Bi/AA gel films, where C=O stretching vibration appears at lower wave numbers ( $1721\text{ cm}^{-1}$ ) and C=C stretching vibration appears at higher wave numbers ( $1638\text{ cm}^{-1}$ ) compared with those of

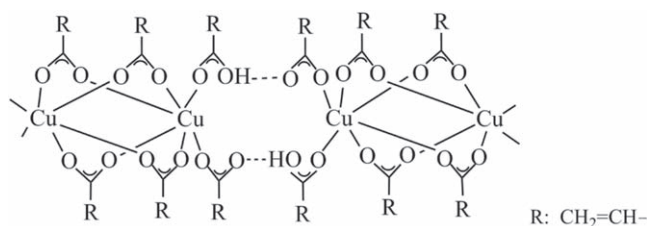


Figure 4. Schematic structure of the Cu complex.

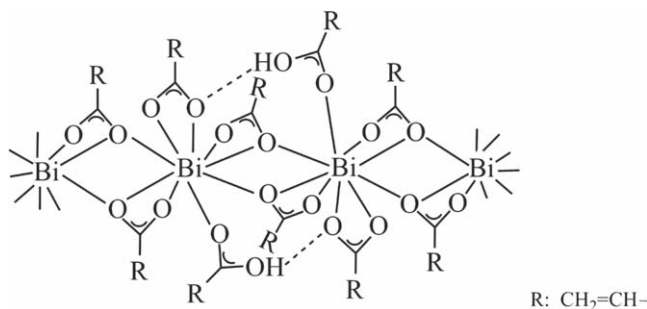
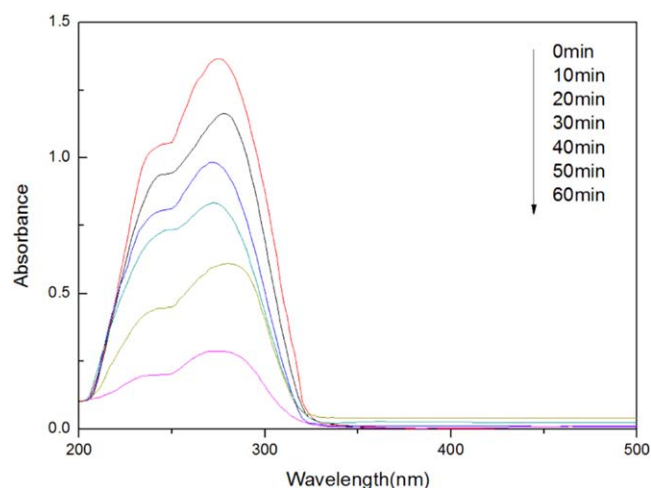


Figure 5. Schematic structure of Bi complex.

AA dissolving in methanol. The FT-IR spectrum also has  $\nu_a(\text{COO}^-)$  at  $1615\text{ cm}^{-1}$  and  $1539\text{ cm}^{-1}$  and  $\nu_s(\text{COO}^-)$  at  $1419\text{ cm}^{-1}$  and  $1360\text{ cm}^{-1}$  [21, 22], and the characteristic peaks at  $670\text{ cm}^{-1}$  and  $501\text{ cm}^{-1}$  are assigned to the Bi-O and Bi-O-Bi stretching vibrations of the Bi complex [23–25]. The above results indicate that a coordination reaction happened between the AA and the Bi ion rather than an ionic reaction. Carboxyl oxygen and hydroxyl oxygen of AA have a strong affinity with Bi ions because metal bismuth has strong metallicity, which results in AA being coordinated with the Bi ions through a deprotonation reaction. FT-IR spectrum of the Bi/AA gel films shows the difference between  $\nu_a(\text{COO}^-)$  and  $\nu_s(\text{COO}^-)$  is about  $200\text{ cm}^{-1}$  [20], it demonstrates that two of the AA groups act as ‘tridentate’ bridging ligands between a bismuth ion and its two symmetry dependant neighbors in the chain [26, 27]. The third AA and the two symmetry dependant neighbors are connected by a strong O-H...O hydrogen bridge. The schematic structure of the Bi complex is illustrated in figure 5.

Figure 3(d) shows FT-IR spectrum of the Bi-2212 gel film, where C=O stretching vibration appears at lower wave numbers ( $1724\text{ cm}^{-1}$ ) and C=C stretching vibration appears at higher wave numbers ( $1644\text{ cm}^{-1}$ ) compared with those of AA dissolving in methanol. The FT-IR spectrum also has  $\nu_a(\text{COO}^-)$  at  $1601\text{ cm}^{-1}$  and  $1550\text{ cm}^{-1}$  and  $\nu_s(\text{COO}^-)$  at  $1433\text{ cm}^{-1}$  and  $1366\text{ cm}^{-1}$ , and their intensity is stronger than that of the  $\text{Cu}(\text{OAc})_2/\text{AA}$  solution and the  $\text{Bi}(\text{OAc})_3/\text{AA}$  solution, which is attributed to the  $\nu_a(\text{COO}^-)$  and  $\nu_s(\text{COO}^-)$  being overlapped after compositing the above four metal solutions [28, 29]. The wide characteristic peak at  $676\text{ cm}^{-1}$  corresponds to the overlap absorption bands of the Cu-O stretching vibration of the Cu complex at  $689\text{ cm}^{-1}$  and the Bi-O stretching vibration of the Bi complex at  $670\text{ cm}^{-1}$ . The spectrum also shows the characteristic peak of Bi-O-Bi stretching vibration at  $543\text{ cm}^{-1}$ .



**Figure 6.** Change in UV-vis absorption spectra with UV irradiation for the Bi-2212 gel films.

According to the measurements of the UV-vis spectra and FT-IR spectra, we conclude that the Bi complex and the Cu complex, which are formed by AA reacting with  $\text{Bi}(\text{OAc})_3$  and  $\text{Cu}(\text{OAc})_2$ , are stable in Bi-2212-sol.

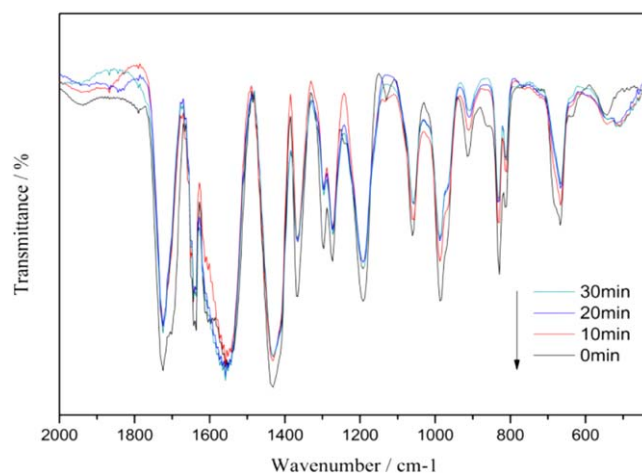
Figure 6 illustrates the change in UV-vis absorption intensity at 246 nm and 270 ~ 280 nm with UV irradiation time. With increasing UV irradiation time, the absorption intensity decreases. These curves demonstrate that metal complexes are photolyzed with the UV irradiation time increases, changing the chemical structure of Bi-2212 films and decreasing the concentration of the metal complexes. The results indicate that Bi complex and Cu complex are stable in Bi-2212-sol, and acrylic acid-modified Bi-2212 gel film is photosensitive.

Figure 7 illustrates the change in IR spectra with UV irradiation for the Bi-2212 gel films. With UV irradiation time increases, characteristic peaks ranging from 2000–600  $\text{cm}^{-1}$  decrease or disappear. Whereas two absorption peaks at 541 and 507  $\text{cm}^{-1}$ , which are attributed to the Cu–O–Cu and Bi–O–Bi stretching vibration, are detected and become stronger. So, we guess that the Bi complex and Cu complex have been photolyzed into inorganics which are insoluble in organic solvent, and the chemical structure of the Bi-2212 gel films has been changed, and the AA-modified Bi-2212 gel films are photosensitive. The photolyzed reactions of the Cu complex and Bi complex are illustrated in figures 8 and 9.

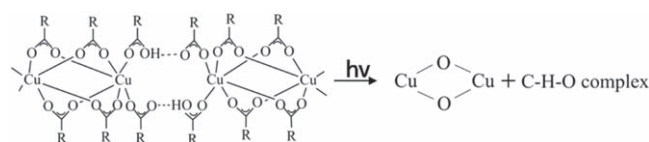
### 3.2. Fine patterns of Bi-2212 thin films

The fine-patterned Bi-2212 gel films were prepared on LAO substrates in room temperature by the fine-patterning process, as shown in figure 1.

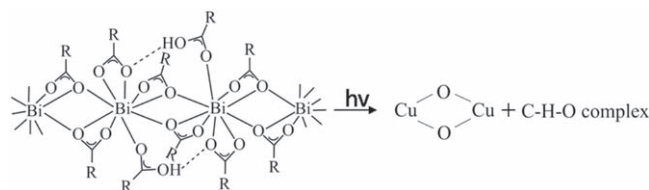
Figure 10 shows an optical microscope photograph of the fine patterns of Bi-2212 films. It can be clearly seen that the black rectangular strips are Bi-2212 thin films. Thus, the negative pattern of the mask was transferred exactly. Every strip can be seen clearly and the smallest width of the dark rectangle strip is roughly 3  $\mu\text{m}$ . Figure 11 shows microarrays of Bi-2212 films with different resolutions (figure 11(a) 5  $\mu\text{m}$  dots, figure 11(b)



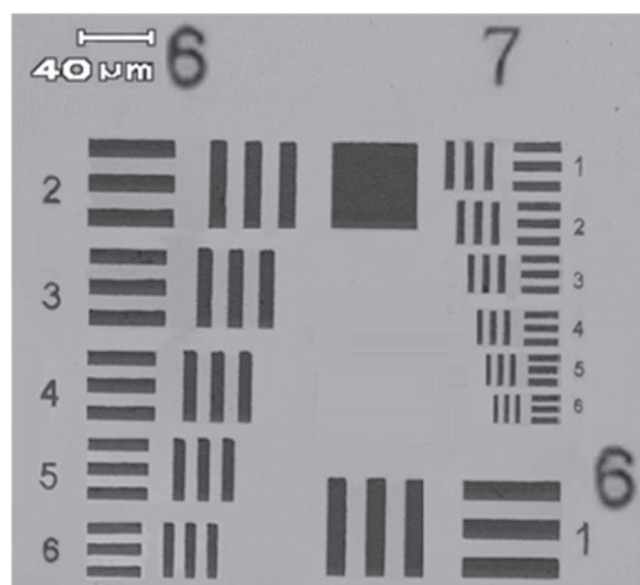
**Figure 7.** Change in IR spectra with UV irradiation for the Bi-2212 gel films.



**Figure 8.** Photolyzed schematic structure of the Cu complex.

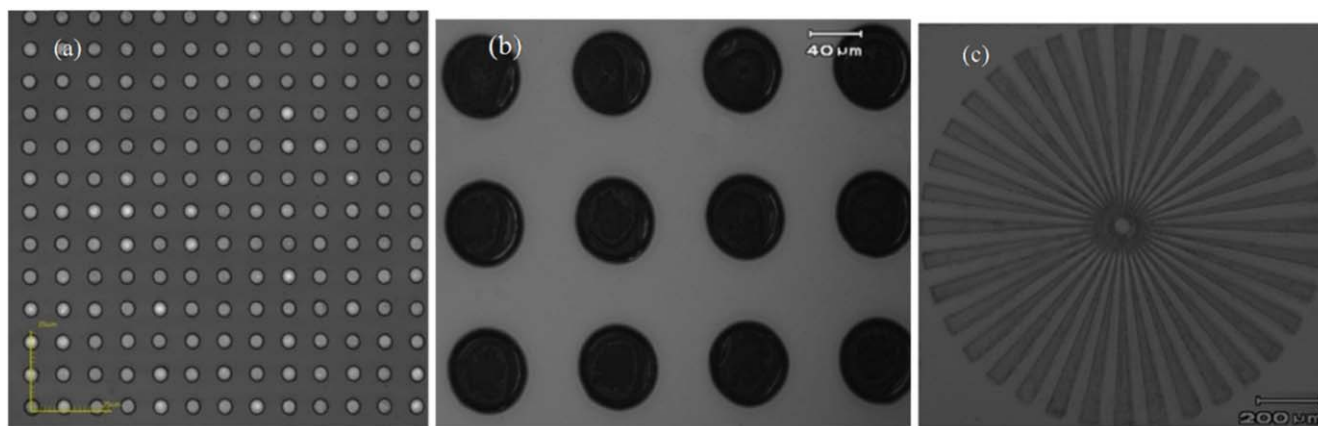


**Figure 9.** Photolyzed schematic structure of the Bi complex.

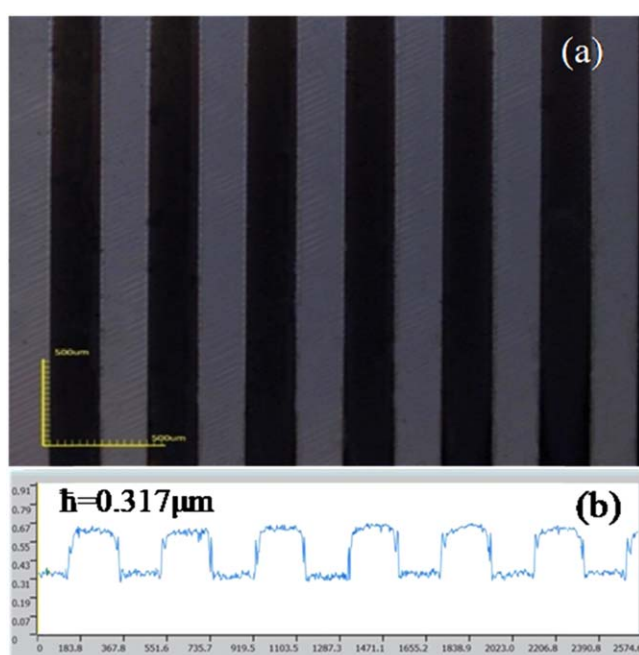


**Figure 10.** Optical microscopy photograph of the fine-patterned Bi-2212 films.

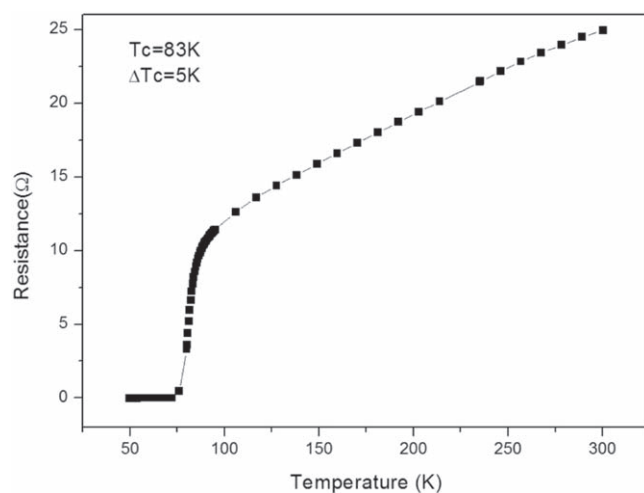




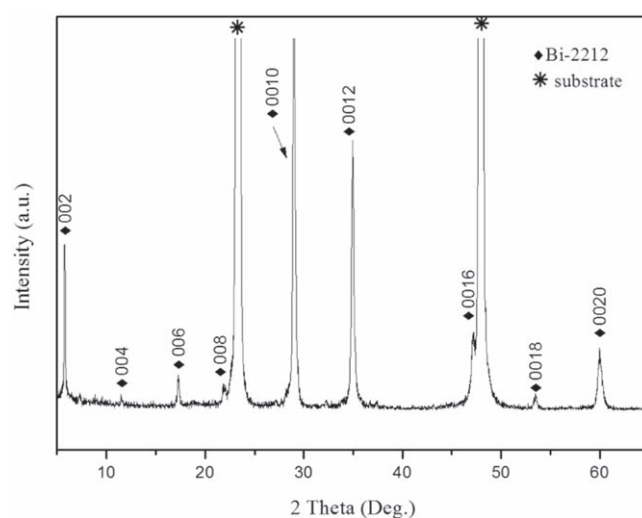
**Figure 11.** Bi-2212 film microarrays with different resolutions (a) 5  $\mu\text{m}$  dots, (b) 50  $\mu\text{m}$  dots, and (c) 10  $\mu\text{m}$  lines.



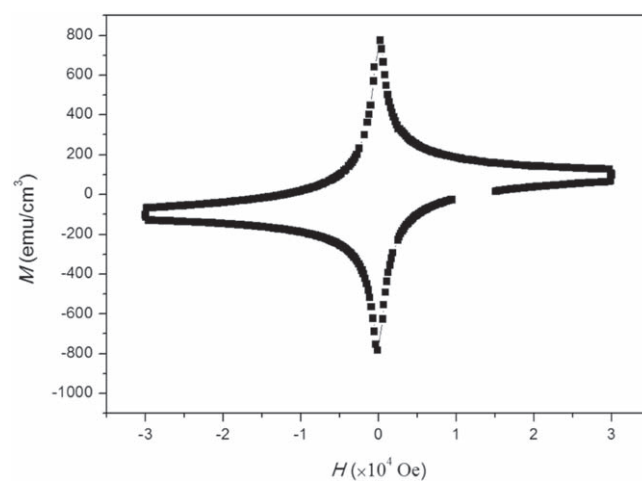
**Figure 12.** LSCM photograph (a) and line profiles (b) of the patterned Bi-2212 films with 200  $\mu\text{m}$  lines.



**Figure 13.**  $R$ - $T$  curves of the fine-patterned Bi-2212 films.



**Figure 14.** XRD patterns of the fine-patterned Bi-2212 films.



**Figure 15.**  $M$ - $H$  curves of the fine-patterned Bi-2212 films.

50  $\mu\text{m}$  dots, and figure 11(c) 10  $\mu\text{m}$  lines). The black regions represent Bi-2212 film.

In order to measure the superconductivity of the fine-patterned Bi-2212 films, Bi-2212 films with 200  $\mu\text{m}$  lines were prepared. Figure 12 illustrates a laser scanning confocal

microscopy (LSCM) photograph and line profiles of the fine-patterned Bi-2212 films with 200  $\mu\text{m}$  lines, with a thickness of about 317 nm. Figure 13 shows the  $R$ - $T$  curves for the Bi-2212 superconducting lines, which exhibit good superconductivity with a critical transition temperature ( $T_c$ ) of 83 K and critical transition width ( $\Delta T_c$ ) of 5 K. Figure 14 shows an XRD pattern of Bi-2212 superconducting lines. As seen, the (002), (006), (008), (0010), (0012), (0016), and (0020) peaks of Bi-2212 were detected. The single Bi-2212 phase was obtained and its growth orientation was on the  $c$ -axis. Figure 15 shows hysteresis loops of the samples measured at 50 K. The critical current density  $J_c$  could be deduced from these loops by use of Bean's critical state model [30]. The value of  $J_c$  for the superconducting lines is  $2.2 \times 10^5 \text{ A cm}^{-2}$  at 50 K under zero magnetic field.

#### 4. Conclusion

A stable transparent blue photosensitive Bi-2212 sol has been successfully synthesized from the methanol of metal acetates with AA. Its photosensitivity and the effects of UV irradiation on their properties were investigated, and subsequently, fine patterns of Bi-2212 gel films were fabricated in an ambient atmosphere. Our conclusions are as follows.

(1) Bi/AA solution and Cu/AA solution have absorption peaks at around 270 ~ 280 nm corresponding to  $\pi$ - $\pi^*$  electron transition of AA in Cu complexes or Bi complexes. (2) The UV irradiation made the metal complexes photolyzed, and changed the chemical structure of the Bi-2212 gel films. Thereby causing the change in solubility of the gel films in organic solvents, and making the Bi-2212 gel films photosensitive. (3) The AA-modified sol-gel method proved the feasibility of one step preparation of fine patterned Bi-2212 gel films, and the fine pattern had the smallest resolution of 3  $\mu\text{m}$ . (4) The prepared fine-patterned Bi-2212 superconducting films have good  $c$ -axis growth orientation and a high  $T_c$  of 83 K and narrow  $\Delta T_c$  of 5 K. Moreover, the  $M$ - $H$  loop shows a  $J_c$  value up to  $2.2 \times 10^5 \text{ A cm}^{-2}$ .

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#### References

- [1] Nishiyama M *et al* 2004 Nanometre-sized inhomogeneity in high- $J_c$   $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$  superconductors *Supercond. Sci. Technol.* **17** 1406–10
- [2] Han K H *et al* 1991 1/f noise in the resistive transition region of high-temperature superconductor YBCO microbridged thin films *Supercond. Sci. Technol.* **4** 677–879
- [3] Minami H *et al* 2009 Characteristics of terahertz radiation emitted from the intrinsic Josephson junctions in high- $T_c$  superconductor  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$  *Appl. Phys. Lett.* **95** 232511
- [4] Ishibashi T *et al* 1999 Submicron-size fabrication of BSCCO thin films by using patterned substrates *IEEE Trans. Appl. Supercond.* **9** 2383–6
- [5] Kakeya I *et al* 2012 Effect of thermal inhomogeneity for terahertz radiation from intrinsic Josephson junction stacks of  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$  *Appl. Phys. Lett.* **100** 242603
- [6] Zhao G and Tohge N 1998 Preparation of photosensitive gel films and fine patterning of amorphous  $\text{Al}_2\text{O}_3$ - $\text{SiO}_2$  thin films *Mater. Res. Bull.* **33** 21–30
- [7] Wu C, Zhao G and Qiao F 2014 Characteristics of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}/\text{SrTiO}_3/\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  films formed by chemical solution deposition *Ceram. Int.* **40** 13145–50
- [8] Zhao G, Zhang W and Du Z 2004 Preparation of  $\text{Pb}_{0.98}\text{La}_{0.02}(\text{Zr}_{0.65}\text{Ti}_{0.35})\text{O}_3$  films and their fine patterning *Mater. Res. Bull.* **39** 449–56
- [9] Kim H-R *et al* 2002 Resistance of superconducting fault current limiters based on  $\text{YBa}_2\text{Cu}_3\text{O}_7$  thin films after quench completion *Physica C* **372–376** 1606–9
- [10] Tsujimoto M *et al* 2015 Terahertz emission from a stack of intrinsic Josephson junctions in Pb-doped  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$  *Supercond. Sci. Technol.* **28** 105015
- [11] Matsui S *et al* 1988 Focused ion beam processed for high- $T_c$  superconductors *J. Vac. Sci. Technol.* **B6** 900–5
- [12] Sobolewski R *et al* 1994 Monolithic Y-Ba-Cu-O structures fabricated using the laser-writing patterning technique *Supercond. Sci. Tech.* **7** 300–3
- [13] Kula W, Xiong W and Sobolewski R 1995 Laser patterning of  $\text{YBa}_2\text{Cu}_3\text{O}_x$  thin films protected by *in situ* grown  $\text{SrTiO}_3$  cap layer *IEEE Trans. Appl. Supercond.* **5** 1177–80
- [14] Lakhani A *et al* 2006 Surface modification in single crystal surface of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  upon high energy ion irradiation *Nucl. Instrum. Methods Phys. Res. B* **244** 120–3
- [15] Liu X *et al* 2018 High efficiency preparation of  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$  superconducting thin films by an acetate based sol-gel process *Mater. Chem. Phys.* **216** 153–7
- [16] Deng Q, Liu L and Deng H 2010 *Spectroscopy Tutorial* (Beijing: Science Press)
- [17] Arun Prasath R *et al* 2006 Synthesis and characterization of poly (urethane-ester) based on calcium salt of mono (hydroxybutyl) phthalate *J. Appl. Polym. Sci.* **100** 1720–7
- [18] Baranauskas A, Jasaitis D and Kareiva A 2002 Characterization of sol-gel process in the Y-Ba-Cu-O acetate-tartrate system using IR spectroscopy *Vib. Spectrosc.* **28** 263–75
- [19] Piro O E, Giiida J A and Massa N E 1989 Infrared reflectivity and vibrational structure of superconducting  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$  *Phys. Rev. B* **39** 7255
- [20] Weng W, Yang J and Ding Z 1994 A complexing approach to inducing sol-gel process of insoluble Cu ethoxide-evolution of local environment of Cu complex species *J. Non-Cryst. Solids* **170** 134–42
- [21] Logutenko O A *et al* 2006 Precipitation of bismuth(III) tartrates from nitrate solutions *Russ. J. Appl. Chem.* **76** 1–6
- [22] Timakova E V, Udalova T A and Yukhin Y M 2009 Precipitation of bismuth(III) salicylates from mineral acid solutions *J. Inorg. Chem.* **54** 873–80
- [23] Lee Y *et al* 2017 A series of bismuth-oxychloride/bismuth-oxyiodide/graphene-oxide nanocomposites: synthesis, characterization, and photocatalytic activity and mechanism *J. Mol. Catal.* **432** 196–209

- [24] Lee W W *et al* 2015 Synthesis of bismuth oxyiodides and their composites: characterization, photocatalytic activity, and degraded mechanisms *RSC Adv.* **5** 23450–63
- [25] Novokreshchenova M N, Yukhin Y and Bokhonov B B 2005 Highly pure bismuth(III) oxochloride synthesis *Chem. Sustain. Dev.* **13** 563–8
- [26] Reiss G J, Frank W and Schneider J 1995 Synthesis and crystal structure of bismuth(III) trifluoroacetate-trifluoroacetic acid adduct,  $\text{Bi}(\text{OOC}\text{CF}_3)_3 \cdot \text{HOOC}\text{CF}_3$  *Main Group Met. Chem.* **18** 287–94
- [27] Ouchi A *et al* 1988 Structure of rare earth carboxylates in dimeric and polymeric forms *Coord. Chem. Rev.* **92** 29–43
- [28] Aranda P *et al* 1995 Composite membranes based on macrocycle/polysiloxanes: preparation, characterization and electrochemical behaviour *Mater. Chem.* **5** 817–25
- [29] Dragan S and Fitch A 1998 Infrared spectroscopy determination of lead binding to ethylenediaminetetraacetic acid *J. Chem. Educ.* **75** 1018–21
- [30] Bean C P 1962 Magnetization of hard superconductors *Phys. Rev. Lett.* **8** 250–3