

ACCEPTED MANUSCRIPT

One step preparation of photosensitive $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$ films and their fine patterns by photosensitive Sol-Gel method

To cite this article before publication: Xiaoqin Liu *et al* 2018 *Supercond. Sci. Technol.* in press <https://doi.org/10.1088/1361-6668/aae8c6>

Manuscript version: Accepted Manuscript

Accepted Manuscript is "the version of the article accepted for publication including all changes made as a result of the peer review process, and which may also include the addition to the article by IOP Publishing of a header, an article ID, a cover sheet and/or an 'Accepted Manuscript' watermark, but excluding any other editing, typesetting or other changes made by IOP Publishing and/or its licensors"

This Accepted Manuscript is © 2018 IOP Publishing Ltd.

During the embargo period (the 12 month period from the publication of the Version of Record of this article), the Accepted Manuscript is fully protected by copyright and cannot be reused or reposted elsewhere.

As the Version of Record of this article is going to be / has been published on a subscription basis, this Accepted Manuscript is available for reuse under a CC BY-NC-ND 3.0 licence after the 12 month embargo period.

After the embargo period, everyone is permitted to use copy and redistribute this article for non-commercial purposes only, provided that they adhere to all the terms of the licence <https://creativecommons.org/licenses/by-nc-nd/3.0>

Although reasonable endeavours have been taken to obtain all necessary permissions from third parties to include their copyrighted content within this article, their full citation and copyright line may not be present in this Accepted Manuscript version. Before using any content from this article, please refer to the Version of Record on IOPscience once published for full citation and copyright details, as permissions will likely be required. All third party content is fully copyright protected, unless specifically stated otherwise in the figure caption in the Version of Record.

View the [article online](#) for updates and enhancements.

**One step preparation of photosensitive Bi₂Sr₂CaCu₂O_{8+x} films and their fine patterns by
photosensitive Sol-Gel method**

Xiaoqin Liu^{a*}, Gaoyang Zhao^{a*}

^a School of Material Science and Engineering, Xi'an University of Technology, Xi'an, 710048, P. R. China

*Corresponding Author. Tel.: +86 15249297943

E-mail: l_xqin@163.com (L. Xiaoqin)

Abstract

An acrylic acid-modified photosensitive Sol-Gel method was proposed to prepare Bi₂Sr₂CaCu₂O_{8+x} (Bi-2212) gel films and their fine patterns on LaAlO₃ (LAO) single crystal substrates. UV-vis absorption spectrum showed the UV characteristic absorption peak at around 270~280 nm which originates from π - π^* electron transition of acrylic acid in metal-complexes, and its intensity decreases with the UV irradiation time increases, indicating that Bi-2212 gel films are photosensitive. Based on the photosensitivity of Bi-2212 gel films, their fine patterns with the smallest resolution of 3 μ m have been prepared. The prepared fine-pattern Bi-2212 superconducting films exhibit c-axis growth orientation and excellent superconducting properties.

Key words: Bi-2212 films, photosensitive Sol-Gel, fine patterns, superconductivity

1. Introduction

Since the discovery of Bi-based superconductors, it has attracted considerable attention, due to its unique physic and structure characteristics such as a high anisotropic and two-dimensionality, a short coherence length, an intrinsic Josephson effects, and without rare earth elements or toxic elements. Bi-2212 high-T_c superconducting films can be widely applied in superconducting microelectronic field on condition that they often need to be fine-patterned [1-5]. In recent years, many efforts in development of fine-pattern technology of films have been performed by our research group, and a photosensitive Sol-Gel method has been progressed. This method provides a new fine-pattern method to high-T_c superconducting films that are applied in superconducting microelectronic devices. [6-8]. Compared with some traditional fine-pattern methods such as Wet Chemical Etching [9], Focused Ion Beam [10-11], Laser Patterning [12-13] and High Energy Ion Irradiation [14], photosensitive Sol-Gel method dramatically reduces surface damage and property degradation resulting from ion beam or etching agent, and realizes the integration and high-efficient of microstructure.

Photosensitive Sol-Gel method combines chemical modification method and sol-gel method. The solutions that modified by chemical modifiers will be photosensitive. When the gel films are irradiated

in air with UV light, resulting in the 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-modified photosensitive Sol-Gel method for Bi-2212 photosensitive sol and their fine patterns has been proposed. The main purpose of the research paper is to use acrylic acid either as 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 acrylic acid. 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-pattern Bi-2212 gel films, fine-pattern Bi-2212 superconducting films can be prepared.

2. Experiment

2.1 Preparation of photosensitive Bi-2212 solution

Analytical reagent $\text{Bi}(\text{CH}_3\text{COO})_3(\text{Bi}(\text{OAc})_3)$, $\text{Sr}(\text{CH}_3\text{COO})_2 \cdot 1/2\text{H}_2\text{O}$ ($\text{Sr}(\text{OAc})_2$), $\text{Ca}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ ($\text{Ca}(\text{OAc})_2$) 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, acrylic acid (AA) and methanol were used as the chemical modifier and solvent to synthesize Bi/AA solution, Sr/AA solution, Ca/AA solution and Cu/AA solution, respectively. Then, with the molar ratio of metallic ions controlled at $\text{Bi}:\text{Sr}:\text{Ca}:\text{Cu}:\text{AA} = 2:2:1:2:40$, mixing the four solutions 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 UV-vis absorption spectra and FT-IR spectra. And their fine patterns were prepared on LAO single crystal substrates by photosensitive sol-gel method. Details of the preparation process of Bi-2212 sol and the heat treatment process of Bi-2212 superconducting thin films have been illustrated in reference.

2.2 Fine patterns of Bi-2212 gel film

Fig. 1 shows the fine-pattern process of Bi-2212 gel films. Photosensitive Bi-2212 gel films were dip-coated on LAO substrates, and dried at 80°C for 1-2min. 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 mixture solution of methanol and isopropyl alcohol in mole ratio of 8:2 for 40-100s. 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 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].

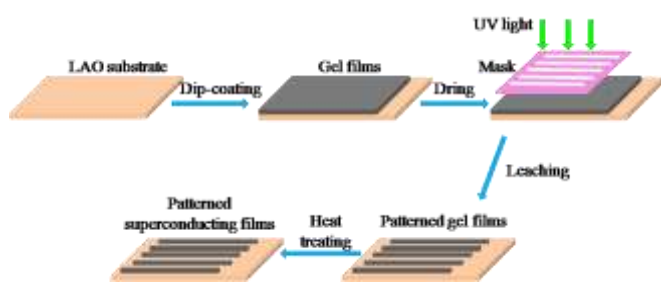


Fig.1 Schematic diagram for the fine-pattern procedure of Bi-2212 films

2.3 Characterization

UV exposure experiments were carried out using a UV spot lamp (250 mW/cm², SP-7-250DB) at room temperature. Fourier transform infrared (FT-IR) spectra of the photosensitive Bi-2212 gel films coated on the silicon wafer were measured with a FT-IR spectrophotometer (IR Prestige-21). The optical absorption spectra of Bi-2212 gel films coated on quartz glass substrates are measured using a UV-vis spectrometer (TU-1901). The phases and crystal orientation of the Bi-2212 films were detected by 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 (Bi³⁺, Cu²⁺) in the solution to form metal-complexes which can absorb UV-vis light, after a certain time of 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 Bi-2212 gel films can be dissolved in organic solvent, the irradiated region is finally remained.

3.1 Photosensitivity of Bi-2212 sol and its gel films

Fig. 2 shows the UV-vis absorption spectra of different solutions. The UV-vis absorption spectrum of acrylic acid dissolving in methanol (AA) with a characteristic absorption peak at around 246 nm which originates from π - π^* electron transition of acrylic acid, as shown in Fig. 2(a) [16].

Fig.2 (b-e) show the UV characteristic absorption spectra of Bi/AA solution, Cu/AA solution, Ca/AA solution and Sr/AA solution, a characteristic absorption peaks at 270~280nm was observed in the UV characteristic absorption spectra of Bi/AA solution and Cu/AA solution, while not observed in that of Ca/AA solution and Sr/AA solution. The appearance of absorption peak at 270~280nm

indicates that some chemical reactions, which change the π - π^* electron transition of acrylic acid, occur in Bi/AA solution and Cu/AA solution.

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

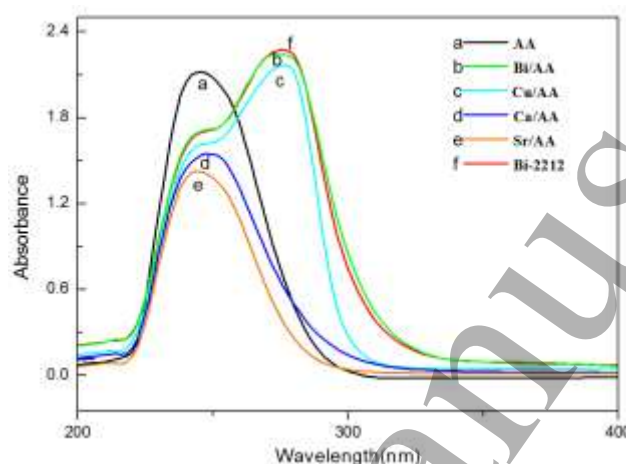


Fig.2 UV-vis absorption spectra for different solutions

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 Fig.3. As seen, the characteristic peak of $\text{C}=\text{O}$ stretching vibration absorption at 1729cm^{-1} was observed in the FT-IR spectrum of AA (Fig.3 (a)), and the non-isomorphic stretching vibrations of $\text{C}=\text{C}$ bond appear at 1636cm^{-1} and 1617cm^{-1} .

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

hydroxyl oxygen atom of acrylic acid provides lone pair electrons to Cu ion, which causes the characteristic peaks of $C=O$ and $C=C$ of acrylic acid shift to lower wave number and higher wave number, respectively.

Fig.3(c) shows FT-IR spectrum of Bi/AA gel films, where $C=O$ stretching vibration appears at lower wave numbers (1721 cm^{-1}) and $C=C$ stretching vibration appears at higher wave numbers (1638 cm^{-1}) compared with that of acrylic acid dissolving in methanol. The FT-IR spectrum also has $\nu_a(\text{COO}^-)$ at 1615 cm^{-1} and 1539 cm^{-1} and $\nu_s(\text{COO}^-)$ at 1419 cm^{-1} and 1360 cm^{-1} [21,22], and the characteristic peaks at 670 cm^{-1} and 501 cm^{-1} are assigned to $\text{Bi}-\text{O}$ and $\text{Bi}-\text{O}-\text{Bi}$ stretching vibrations of Bi-complex [23-25]. The above results indicate that coordination reaction happened between acrylic acid and Bi ion rather than ionic reaction. Carboxyl oxygen and hydroxyl oxygen of acrylic acid have strong affinity with Bi ion because of metal bismuth has strong metallicity, which results in acrylic acid is coordinated with Bi ion through deprotonation reaction. FT-IR spectrum of Bi/AA gel films shows the difference between $\nu_a(\text{COO}^-)$ and $\nu_s(\text{COO}^-)$ is about 200 cm^{-1} [20], it demonstrates that two of the acrylic acid groups act as 'tridentate' bridging ligands between a bismuth ion and its two symmetry dependant neighbours in the chain [26-27]. The third acrylic acid and the two symmetry dependant neighbours are connected by a strong $\text{O}-\text{H}\cdots\text{O}$ hydrogen bridge. The schematic structure of Bi-complex is illustrated in Fig.5.

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

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

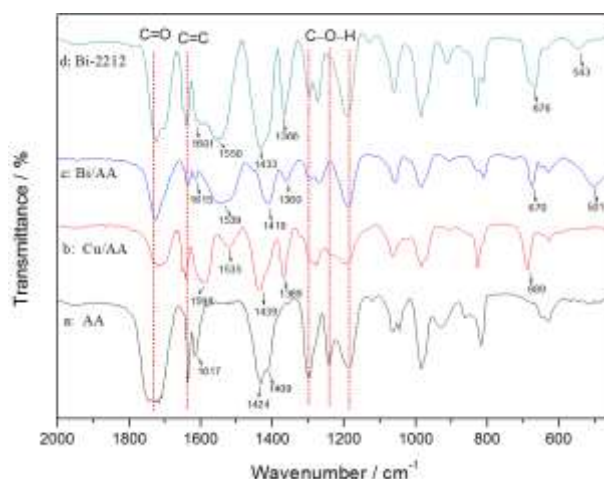


Fig. 3 IR spectra of several gel films

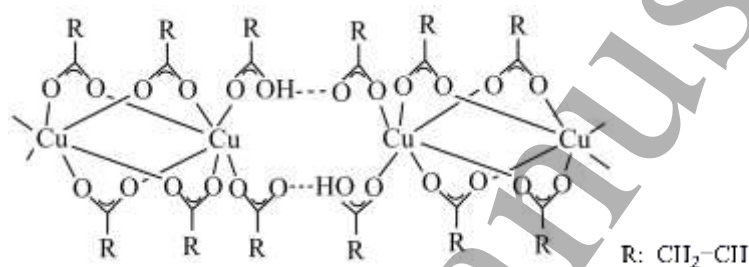


Fig.4 Schematic structure of Cu-complex

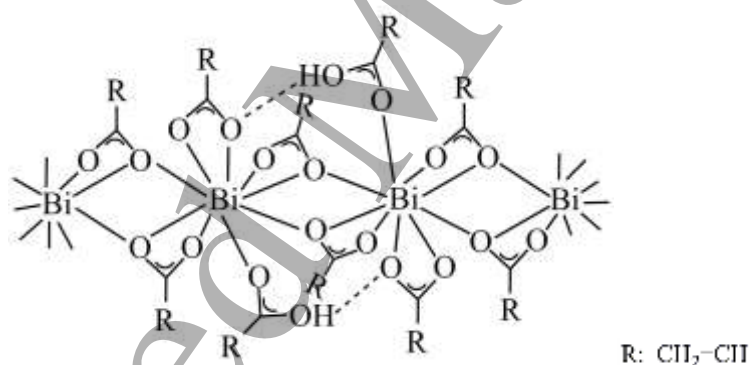


Fig.5 Schematic structure of Bi-complex

Fig.6 illustrates the change in UV-vis absorption intensity at 246nm and 270~280nm 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.

Fig.7 illustrates the change in IR spectra with UV irradiation for Bi-2212 gel films. With UV irradiation time increases, characteristic peaks ranging from 2000 cm⁻¹ to 600cm⁻¹ decrease or

disappear. Whereas two absorption peaks at 541 cm^{-1} and 507 cm^{-1} , which are attributed to the $\text{Cu} - \text{O} - \text{Cu}$ and $\text{Bi} - \text{O} - \text{Bi}$ stretching vibration, are detected and become stronger. So, we guess that Bi-complex and Cu-complex have been photolyzed into inorganics which are insoluble in organic solvent, and the chemical structure of Bi-2212 gel films has been changed, and acrylic acid modified Bi-2212 gel films are photosensitive. The photolyzed reaction of Cu-complex and Bi-complex are illustrated in Fig.8 and Fig.9.

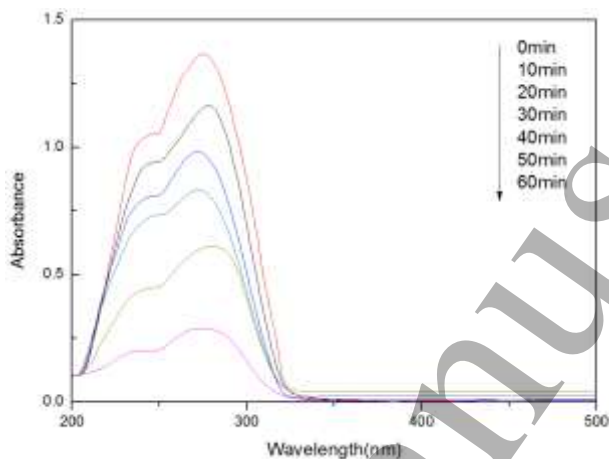


Fig.6 Change in UV-vis absorption spectra with UV irradiation for Bi-2212 gel films

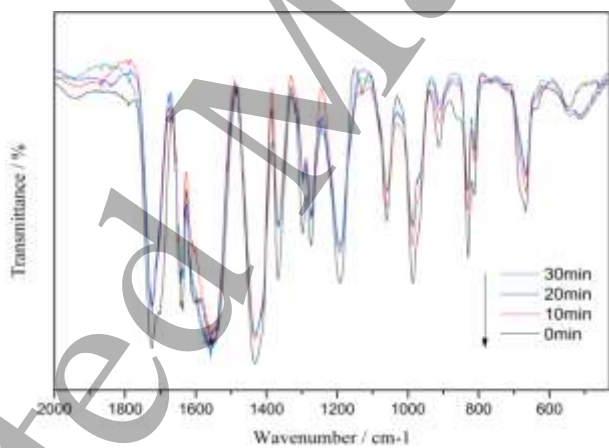


Fig.7 Change in IR spectra with UV irradiation for Bi-2212 gel films

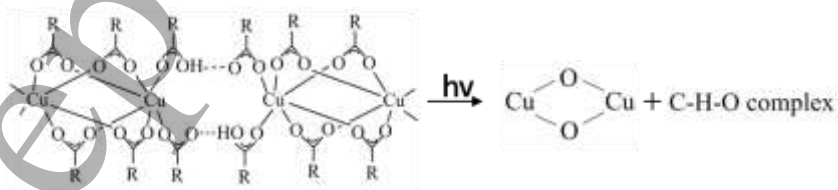


Fig.8 Photolyzed schematic structure of Cu-complex

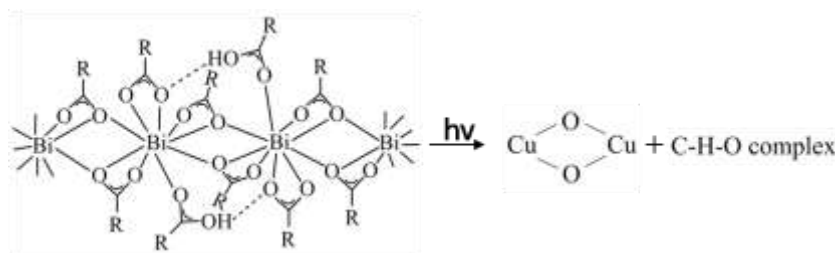


Fig.9 Photolyzed schematic structure of Bi-complex

3.2 Fine patterns of Bi-2212 thin films

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

Fig. 10 shows the 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 $3\mu\text{m}$. Fig. 11 shows the Bi-2212 film's microarrays with different resolution (Fig. 11(a) $5\mu\text{m}$ dots, Fig. 11(b) $50\mu\text{m}$ dots, Fig. 11(c) $10\mu\text{m}$ lines). The black regions represent Bi-2212 film.

In order to measure the superconductivity of fine-pattern Bi-2212 films, Bi-2212 films with $200\mu\text{m}$ lines were prepared. Fig.12 illustrates the Laser Scanning Confocal Microscopy (LSCM) photograph and line profiles of the fine-pattern Bi-2212 films with $200\mu\text{m}$ lines, they have about 317 nm thickness. Fig.13 shows the R-T curves for Bi-2212 superconducting lines, which exhibit good superconductivity with critical transition temperature (T_c) of 83 K and critical transition width (ΔT_c) of 5 K . Fig. 14 shows XRD pattern of Bi-2212 superconducting lines. As seen, (002), (006), (008), (0010), (0012), (0016), (0020) peaks of Bi-2212 were detected. The single Bi-2212 phase was obtained and its growth orientation was c-axis. Fig. 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.

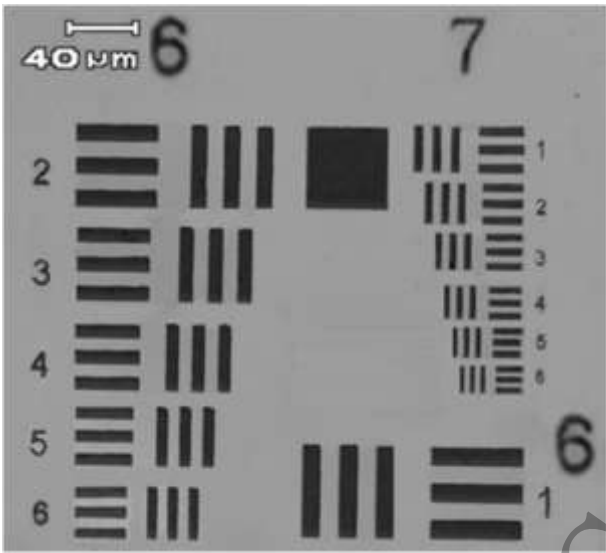


Fig. 10 Optical microscopy photograph of the fine patterned Bi-2212 films

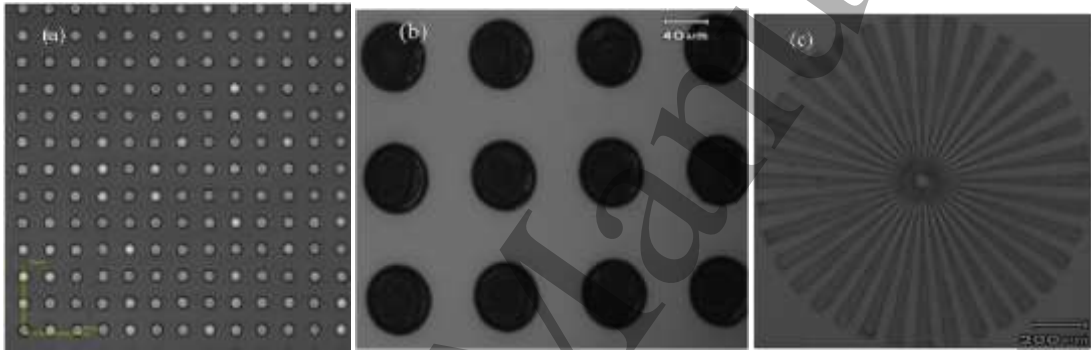


Fig.11 Bi-2212 film's microarrays with different resolution (a) 5μm dots, (b) 50μm dots, (c) 10μm lines

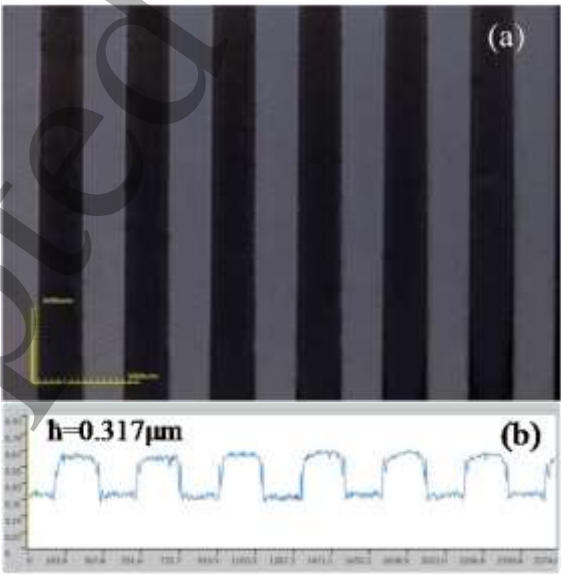


Fig.12 LSCM photograph (a) and line profiles (b) of the patterned Bi-2212 films with 200μm lines

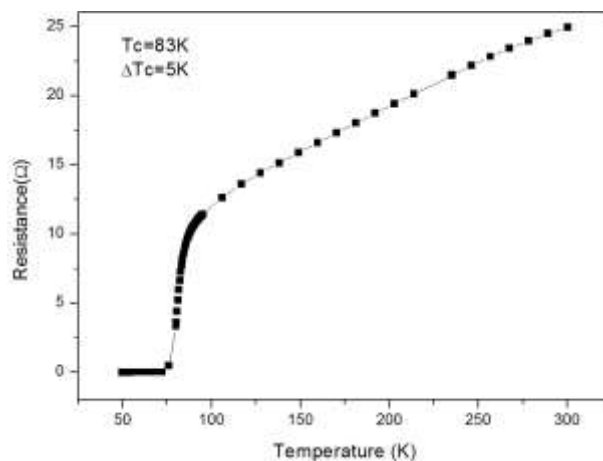


Fig. 13 R-T curves of fine-pattern Bi-2212 films

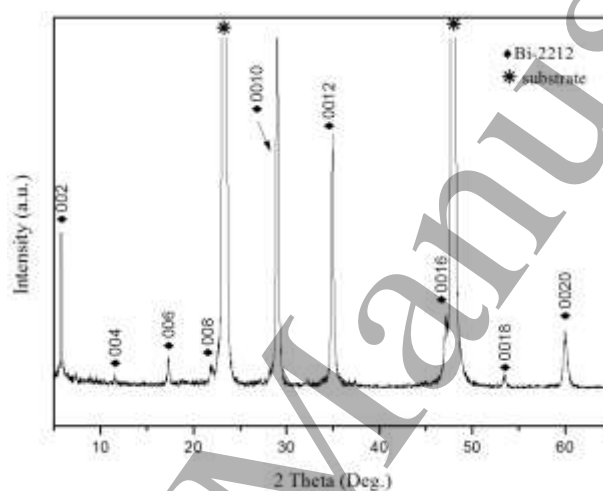


Fig. 14 XRD patterns of fine-pattern Bi-2212 films

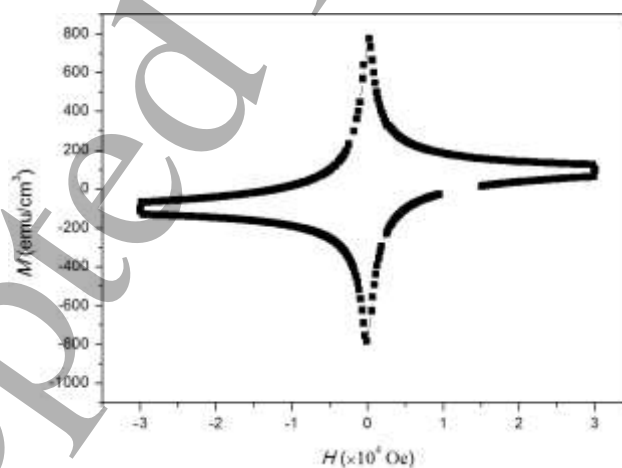


Fig.15 M-H curves of fine-pattern Bi-2212 films

4. Conclusion

A stable transparent blue photosensitive Bi-2212 sol has been successfully synthesized from methanol of metal-acetates with acrylic acid. 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. The conclusions were as follows:

(1) Bi/AA solution and Cu/AA solution have an absorption peaks at around 270~280nm corresponding to π - π^* electron transition of acrylic acid in Cu-complexes or Bi-complexes. (2) The UV irradiation made the metal-complexes photolyzed, and changed the chemical structure of Bi-2212 gel films. Thereby causing the change in solubility of the gel films in organic solvents, and making the Bi-2212 gel films are photosensitive. (3) Acrylic acid modified Sol-Gel method proved the feasibility of one step preparation of Bi-2212 gel films their fine patterns, and the fine pattern had the smallest resolution of 3 μ m. (4) The prepared fine-pattern Bi-2212 superconducting films have good c-axis growth orientation and high T_c of 83K and narrow Δ T_c of 5K. Moreover, M-H loop shows J_c-value up to 2.2×10^5 A/cm².

Acknowledgments

This project is supported by the National Natural Science Foundation of China (No. 51672212).

Reference

- [1] M. Nishiyama, G. Kinoda, Y. Zhao, et al., Nanometre-sized inhomogeneity in high-J_c Bi₂Sr₂CaCu₂O_{8+ δ} superconductors, *Supercond. Sci. Technol.*, 17 (2004) 1406–1410.
- [2] K. H. Han, S. Lee, S. H. Lee, et al., 1/f noise in the resistive transition region of high-temperature superconductor YBCO microbridged thin films, *Supercond. Sci. Technol.*, 4(1631)677-879.
- [3] H. Minami, I. Kakeya, H. Yamaguchi, *et al.*, Characteristics of terahertz radiation emitted from the intrinsic Josephson junctions in high-T_c superconductor Bi₂Sr₂CaCu₂O_{8+ δ} , *Appl. Phys. Lett.*, 95 (2009)232511.
- [4] T. Ishibashi, T. Kawahara, H. Iianeko, *et al.*, Submicron-size Fabrication of BSCCO Thin Filmsbby using Patterned Substrates. *IEEE Tran. Appl. Supercond.*, 9(2)(1999)2383-2386.
- [5] I. Kakeya · Y. Omukai · T. Yamamoto, *et al.* Effect of thermal inhomogeneity for terahertz radiation from intrinsic Josephson junction stacks of Bi₂Sr₂CaCu₂O_{8+ δ} . *Appl. Phys. Lett.*, 100(2012)242603.
- [6] G. Zhao, N. Tohge, Preparation of photosensitive gel films and fine patterning of amorphous Al₂O₃-SiO₂ thin films, *Mater. Res. Bull.*, 33(1) (1998) 21-30.
- [7] C. Wu, G. Zhao, F. Qiao. Characteristics of YBa₂Cu₃O_{7-x}/SrTiO₃/YBa₂Cu₃O_{7-x} films formed by

- chemical solution deposition, *Cera. Int.*, 2014, 40: 13145-13150.
- [8] G. Zhao, W. Zhang, Z. Du, 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 (2004) 449–456
- [9] Hye-Rim Kim, Hyo-Sang Choi, Hae-Ryong *et al.*, 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(2002) 1606-1609.
- [10] M. Tsujimoto, Y. Maeda, H. Kambara, *et al.*, 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(2015)105015.
- [11] S. Matsui, Y. Ochiai, Y. Kojima, *et al.*, Focused ion beam processed for high- T_c superconductors, *J. Vac. Sci. Technol.*, B6(1988)900-905.
- [12] R. Sobolewski, W. Xiong, W. Kula, *et al.*, Monolithic Y-Ba-Cu-O structures fabricated using the laser-writing patterning technique, *Supercond. Sci. Tech.*, 7(1994)300-303.
- [13] W. Kula, W. Xiong, R. Sobolewski, Laser Patterning of $\text{YBa}_2\text{Cu}_3\text{O}_x$ thin films protected by in-situ Grow SrTiO_3 Cap Layer, *IEEE Tran. Appl. Supercond.*, 5(2)(1995)1177-1180.
- [14] A. Lakhani, V. Ganesan, S. Elizabeth, *et al.*, Surface modification in single crystal surface of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ upon high energy ion irradiation, *Nucl. Instrum. and Meth. in Phys. Res. B*, 244(2006) 120-123.
- [15] X. Liu, G. Zhao, L. Lei, *et al.*, 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 (2018) 153–157.
- [16] Q. Deng, L. Liu, H. Deng, *Spectroscopy Tutorial* [M]. Beijing, China: Science Press., 2010.
- [17] R. Arun Prasath, S. Nanjundan, T. Pakula, *et al.*, Synthesis and Characterization of Poly (urethane-ester) Based on Calcium Salt of Mono (hydroxybutyl) phthalate, *J. Appl. Polym. Sci.*, 100(3)(2006)1720-1727.
- [18] A. Baranauskas, D. Jasaitis, A. Kareiva, Characterization of Sol-Gel process in the Y-Ba-Cu-O acetate-tartrate aystem using IR spectroscopy, *Vibration Spec.*, 28(2002)263-275.
- [19] Oscar E. Piro, J. A. Giiida, N. E. Massa, Infrared reflectivity and vibrational structure of superconducting $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$, *Phys Rev.*, B39(10)(1989)7255.
- [20] W. Weng, J. Yang, Z. Ding, 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(1994)134-142.
- [21] O. A. Logutenko, V. I. Evseenko, Yu. M. Yukhin, *et al.*, Precipitation of Bismuth(III) Tartrates from Nitrate Solutions. Russ. J. Appl. Chem. 76(1)(2006)1-4.
- [22] E. V. Timakova, T. A. Udalova, Yu. M. Yukhin, Precipitation of bismuth(III) salicylates from mineral acid solutions, J. Inorg. Chem., 54(6)(2009)873-880.
- [23] Y. Lee, Y. Dai, J. Fu, *et al.*, A series of bismuth-oxychloride/ bismuth-oxiodide/ graphene-oxide nanocomposites: Synthesis, characterization, and photocatalytic activity and mechanism, J. Molecu. Catal., 432(2017)196-209.
- [24] W. W. Lee, C. S. Lu, C. W. Chuang, *et al.*, Synthesis of Bismuth Oxyiodides and Their Composites: Characterization, Photocatalytic Activity, and Degraded Mechanisms, RSC Adv., 5(2015)23450-23463.
- [25] M. N. Novokreshchenova, Y. Yukhin, B. B. Bokhonov, Highly pure bismuth(III) oxochloride synthesis, Chem. Sustainable Dev., 13(2005)563-568.
- [26] G. J. Reiss, W. Frank, J. Schneider, 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(6)(1995)287-294.
- [27] A. Ouchi, Y. Susuki, Y. Okhi, *et al.*, Structure of rare earth carboxylates in dimeric and polymeric forms, Coord. Chem Rev. 92(1988)29-43.
- [28] P. Aranda, A. Jiménez-Morales, J. Carlos Galvan, *et al.*, Composite Membranes based on Macrocyclic/Polysiloxanes: Preparation, Characterization and Electrochemical Behaviour, Mater. Chem., 5(6) (1995)817-825.
- [29] S. Dragan, A. Fitch, Infrared Spectroscopy Determination of Lead Binding to Ethylenediaminetetraacetic Acid, Chem. Edu., 75(8)(1998)1018-1021.
- [30] C.P. Bean, Magnetization of hard superconductors, Phys. Rev. Lett., 8 (1962)250-253.