Using Non-Fluorine Precursor to Prepare YBCO Thin Films by Chemical Solution Deposition

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Abstract. A fluorine-free chemical solution deposition route has been established for YBCO thin films which is inexpensive and environmentally friendly. The YBCO precursor was formed by dissolving the YBCO powder in organic acid and polymer. Amine is used to modify the solution. Several routes with different reagents have been investigated. For the preparation of YBCO thin films, a thin precursor film was coated on single crystal substrate by dip-coating and burnt out on a hotplate in air followed by annealing in a tube furnace with low oxygen pressure argon atmosphere. The films have been characterised by XRD and SEM and the superconducting properties measured by AC susceptibility. The effect of annealing temperature and oxygen partial pressure has been studied.

1. Introduction
Different deposition methods have been successfully used to prepare YBa$_2$Cu$_3$O$_{7-\delta}$(YBCO) films, such as pulsed laser deposition (PLD), e-beam, chemical vapour deposition. Compared with these vapour depositions, chemical solution deposition (CSD) is a non-vacuum and high speed deposition method which is more suitable for industry. Trifluoroacetates metalorganic deposition (TFA-MOD)[1] is the most popular chemical solution deposition for YBCO thin films, which can produce high $J_c$ superconducting films. But TFA method uses water to decompose the BaF$_2$ and results in highly corrosive HF gas. There are also some non fluorine precursors which have been prepared for YBCO films which can avoid the HF gas. Among these precursors, carboxylate[2-4], acetylacetonates[5], triethanolamine[6], naphthenates[7], and polymer[8] were used for Y,Ba,Cu solutions.

A new non-fluorine precursor was developed by dissolving YBCO powder in butyric acid and poly amine was used to modify the precursor. This precursor can be prepared in simple conditions from common inexpensive reagents and the solution can be stable for several months.

2. Experimental
YBCO powder dissolved in organic acid can produce Y,Ba,Cu carboxylates easily. This is a simple way to get the YBCO precursor for the laboratory without introducing other unnecessary compounds. Formic acid, acetic acid, propionic acid and butyric acid were tried to produce Y,Ba,Cu carboxylic acid solution. It was found that copper butyrate has a higher decomposition temperature than the other
three kinds of copper carboxylates during the vacuum distillation. For this reason, butyrate was used to develop the YBCO precursor.

The YBCO powder was prepared by a standard solid state reaction. A stoichiometric amount of Y₂O₃, BaCO₃, CuO (all from Aldrich, 99.9%) were mixed together and calcined at 900 °C for 10 hours. The mixture was milled into powder at room temperature and this procedure was repeated 9 times. 2.5g of this prepared YBCO powder was dissolved in 20ml butyric acid in a flask and refluxed under 110 °C for 24 hour to get a dark green colour solution. 0.5g polyethyleneimine (M.W. 1800, Alfa) diluted by 20ml distilled water was added to the solution. The solution was concentrated to about 7ml by vacuum distillation. Xylene was used as a solvent and diluted the solution to about 30ml. The solution was kept in a glass bottle as the YBCO precursor. There was no evidence of precipitates found for several months.

Two kinds of single crystal substrates were used directly without any cleaning. LAO substrate is 10mmX5mm, STO substrate is 5mmX5mm. The withdrawal speed of dip-coating is 2cm/min. The coated film was dried on a hotplate at 180°C for 5 minutes and was transferred to another hot plate to burn out the organic compound at 370°C for 30 minutes. Both heat treatments were in air. This procedure was repeated 5 times to increase the film thickness.

The high temperature treatment is depicted in Figure 1. The film was heated up from room temperature to 835°C by 6.7°C/min in low oxygen partial pressure P₀₂=5×10⁻⁴ atm. The film was dwelled for 1 hour at 835°C and cooled down step by step to room temperature. When the furnace temperature reached to 600°C, the atmosphere gas was changed into pure oxygen till room temperature. Various oxygen partial pressures were also used for film heat treatments.

![Figure 1. Schematic diagram of heating treatment for YBCO film](image)

The surface morphology of the film was observed by SEM(JEOL 7000) and a Philip X-ray diffractometer was used for θ-2θ scan.

3. Results and discussion

**Precursor**: the precursor can be prepared with higher concentration to reduce the coating times, In order to reduce the viscosity of the precursor ethanolamine and triethanolamine also were tried for the precursor instead of the polyethyleneimine, but the surface of the YBCO film is too rough to repeat the coating. Unlike other precursors used before, this precursor can only be dip-coated on new single
crystal substrates without any cleaning. If both the new LAO and STO substrates were cleaned by organic solvent followed by heat treatment in furnace[9], the wettability of the precursor is low on these cleaned substrates unless the cleaned substrates were kept in air for more than two weeks before coating. The reason for this is still not clear.

**Processing:** For certain thickness YBCO film growth, low oxygen partial pressure (Po2) and high annealing temperature are favourable for c-axis orientation [10-12]. But the YBCO phase instability at very low Po2 and high temperature are the limitations. In order to optimize the processing, three different oxygen partial pressures were chosen to form the YBCO film during the heat treatment in tube furnace: a) pure argon at 790°C, b) Po2 =5×10\(^{-4}\) atm at 835°C, c) pure O2 at 920°C. The SEM images of different Po2 samples are shown in Figure 2.

It can be observed that the YBCO still has amorphous phase at 790°C(Figure 2a) in pure argon and the grains do not cover all the area. At 920°C(Figure 2c) in pure O2 the intermediate liquid phase was formed and results in higher surface roughness. These results are similar to other reported results[13]. Both of these two samples are non superconducting films. The 835°C sample (Figure 2b) is a superconducting film with a sharp transition at 91K as seen in Figure 3.

**YBCO film:** Butyrate precursor was successfully transformed to an YBCO film on LAO and STO single crystal substrates at low Po2. The XRD pattern of an YBCO film sample coated 6 times on LAO shows strong (00l) peaks (Figure 4) which indicates the film has good c-axis orientation. No other phase can be found. The sample has mirror-like surface to the naked eye. Its SEM image (Figure 2b) shows crack-free film except several voids.
4. Conclusion
Superconducting YBCO films were successfully formed by dip-coating from a new non-fluorine precursor. The preparation of the precursor is inexpensive and environmentally friendly. Different oxygen partial pressures were tried during the heat treatment and low Po2 is necessary to get the superconducting film. The YBCO film is smooth and crack-free and has a Tc=91K.

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