Dip-coated $YBa_2Cu_3O_{7-x}$ films on Ag substrate by MOD method

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The metal organic deposition (MOD) process of $YBa_2Cu_3O_{7-x}$ (YBCO) using metal trifluoroacetates (TFA) precursors is considered to be a strong candidate as a low cost fabrication process in coated conductors since the TFA-MOD process is a non vacuum process and can provide high J_c films. Metal organic deposition using trifluoroacetates (TFA-MOD) with dip coating was applied for the preparation of YBCO films. The thickness of films increases with the withdrawal speed of substrates. In this work, a triple coated film was fabricated on Ag {110}<110> textured polycrystalline substrate by optimizing the condition of heat treatments in the multi-coating method. The YBCO films have J_c value of 15000A/cm^2 (77K, 0T) measured by the four-probe-method.

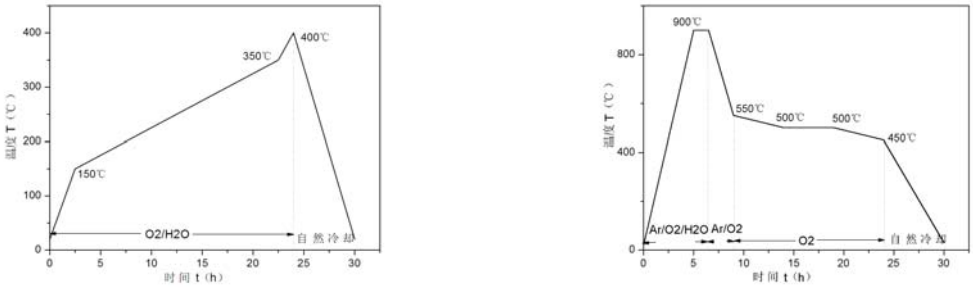
INTRODUCTION

The metal organic deposition (MOD) process of YBCO using metal trifluoroacetates precursors is considered to be a strong candidate as a low cost process of coated conductors, since the TFA-MOD process is basically a non vacuum method. Additionally, it has been well confirmed that this process has an advantage to provide a high J_c film of the MA/cm^2 [1] class on the single crystal substrates such as $LaAlO_3$ and $SrTiO_3$ [2] and on the Ni tapes with multi buffer-layer [3]. But, they are difficult to make long single crystal substrates and to make the Ni tapes with multi buffer-layer. We deposited directly YBCO film on Ag {110}<110> textured polycrystalline substrates to solve the above problem, because it is easy to make long Ag substrate with bi-axially texture. On the one hand, in order to develop long tape conductors, it is important to investigate the influence of dip-coating process on YBCO films. On the other hand, in order to obtain high I_c, processing for thicker YBCO films was investigated using the multi-coating method.

EXPERIMENT

A solution was prepared by dissolving the acetates of Y, Ba, and Cu into de-ionized water in a 1:2:3 cation ratio with stochiometric quantity of TFA, and then water and acetic acid were removed by an evaporator to yield a blue glassy residue. The above residue was put into oven at 100℃ for 10 hours to remove water and acetic acid as absolutely as possible. Dissolving the gel into methanol made the coating solutions that had total metallic concentration of 2.0mol/l. The gel films were coated onto the polished Ag substrates by dip coating. A withdrawal speed of 1.2-5.7mm/s was used for coating gel films. The heat

treatment was conducted by two stages, which were the low temperature treatment and the successive high temperature treatment. The temperature profiles of the heat treatment are showed in figure 1. In the low temperature treatment, the TFA solution precursor films were decomposed to the mixture consisted of amorphous, oxide, fluoride and oxy-fluoride etc. during slowly heating to 400℃ in a moist O_2 atmosphere. In the multi-coating case, after the first low temperature treatment, TFA precursor solution coating was carried out again on the first precursor films. In the high temperature treatment, the films were first heated up to 400℃ in a dry mixed gas of Ar/O_2 and heated to 900℃ in a wet mixed gas of Ar/O_2 and held for about 90 minutes at 900℃ and cooled in a dry gas to the room temperature.



(a) (b)

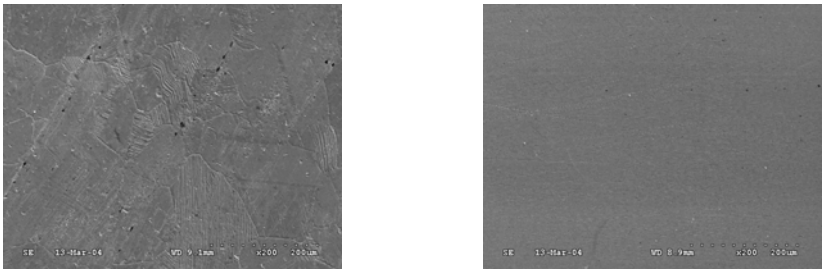
Fig. 1. The heating profiles of (a) Low-temperature heat treatment
(b) High-temperature heat treatment

Crystalline phases in the films were detected by X-ray diffraction. SEM was used to evaluate the surface morphology of films. T_c and J_c were measured using a standard four-probe method at 77K in self-field.

RESULTS AND DISCUSSION

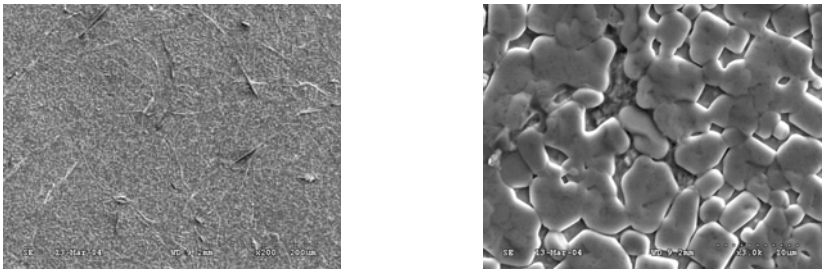
Influence of the polished and unpolished Ag substrates on YBCO films

Fig.2 shows SEM images of Ag substrates. As shown in these figures, the surfaces are different between (a) and (b). The surface of unpolished Ag is rough. Rolling stripes and crystal boundaries could be seen. On the other hand, the mechanically polished Ag is rather smooth. But the epitaxial growth of YBCO films on substrates is affected strongly by the substrate surface [4]. The influences are shown in Fig.3 and Fig.4 clearly. YBCO grain size, secondary phase particles and pores on the surface of each sample are different. As shown in Fig.3 (a), the surface is not smooth and has many stripes like tree for the rolling stripes and crystal boundaries on unpolished Ag substrates. Comparing Fig.3 (b) with Fig.4 (b), there are many large grains and pores in Fig.3 (b). It means that the connections among YBCO grains are bad and there are fewer chances to form the access of electric current. So polished Ag substrates are more available to grow YBCO films.



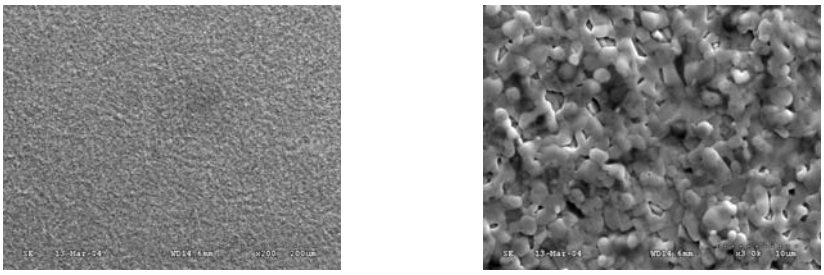
(a) (b)

Fig.2. SEM images of Ag substrates: (a) unpolished and (b) mechanically polished



(a) (b)

Fig.3. SEM images of YBCO films on unpolished Ag substrates: (a) 200× and (b) 3000×



(a) (b)

Fig.4. SEM images of YBCO films on polished Ag substrates: (a) 200× and (b) 3000×

The ageing time of the sol solution

In this work, the sol solution, which will be coated, should be lay aside for at least 3-10 days. If the sol solution has not pass through this process, the gel film is easy to crack. It is mainly because the new-made sol is not stable, sol and gel have not achieve equilibrium. On the other hand, by dip coating method, the sol solution should have a certain extent viscosity [5]. The viscosity of new-made sol is too low to make films what we expect. But, when the sol solution is lay aside for long time, the viscosity of it is too high and the fluidness of it is bad. Then, gel films coated by it are inhomogeneous and easy to have small cracks. So, this process is very necessary.

Influence of the withdrawal speed of Ag substrates on YBCO films

According to the theory of dip coating [5], the thickness of YBCO films (t) is proportional to the square root of the withdrawal speed (v). When the thickness exceeds the critical value, YBCO films will crack. Controlling the withdrawal speed is equal to control the thickness of films. On the one hand, when the withdrawal speed is lower, coating film is thinner and homogeneous at a time. It is necessary that TFA precursor solution is coated again on the first precursor films to make the thicker films. On the other hand, when the withdrawal speed is too high, single dip-coating film is so thick as to crack during successive drying and calcinations process. So, it is important to search and confirm the better withdrawal speed to make the better films.

In this work, four different speeds from 1.2mm/s to 5.7mm/s were adopted. The former three films were dark and homogeneous but the last film had cracks for the high withdrawal speed. The YBCO films prepared on polished Ag substrates by TFA-MOD with dip coating show highly c-axis orientation. In

Fig.5, XRD patterns show that the intensity of the (00l) peaks is strong and sharp and pure. There are no BaF_2 and the other impurities. The intensity of the YBCO peaks increases with increasing withdrawal speed of Ag substrates.

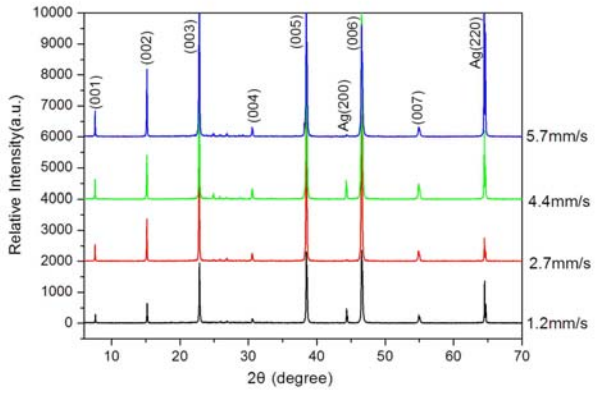
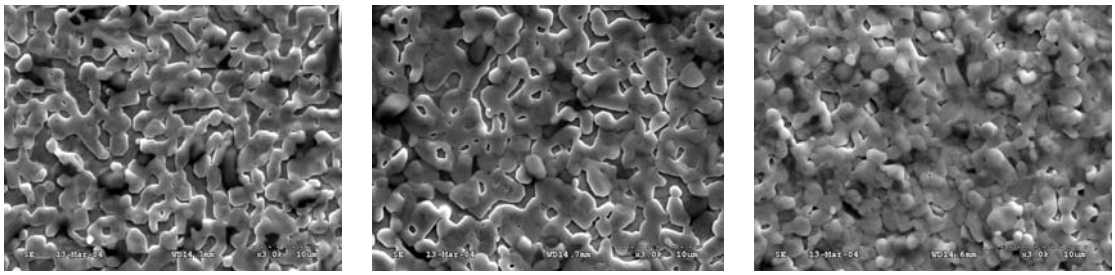


Fig.5. XRD patterns of YBCO thin films on polished Ag substrates

In Fig.6, SEM images show, from a top view, that the YBCO films appear to have a multi-grain structure. With increasing withdrawal speed of Ag substrates, there are more and more joints, fewer and fewer pores among grains. The film with 4.4mm/s withdrawal speed is very dense and homogeneous. So, the withdrawal speed of 4.4mm/s is what we want.



1.2 mm/s 2.7 mm/s 4.4 mm/s

Fig.6. the top surface microstructures for the YBCO samples prepared at different withdrawal speed of polished Ag substrates.

CONCLUSION

We can successfully obtain crack-free YBCO films, which have a J_c value of 15000A/cm^2 (77K, 0T), on Ag {110}<110> textured polycrystalline substrate, by optimizations of the TFA-MOD process: preparation of coating solutions and other processes, including coating, calcining, firing processes and humidity control. The mechanically polished Ag substrates are better for the growth of YBCO films than unpolished Ag substrates. The sol solution should be lay aside for several days to coat YBCO films well. However, considering the future engineering application, it is further required to optimize TFA-MOD method to improve J_c of YBCO films.

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