ELECTRODEPOSITION OF HIGH- T_c SUPERCONDUCTOR MATERIAL FOR MICROSENSOR FABRICATION

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ABSTRACT

Thin-films of $YBa_2Cu_3O_7$ (YBCO) superconductor precursor were synthesized using an electrodeposition process. The YBCO precursor thin films were deposited on Ag foils using pulsed potential deposition conditions of 10 s at - 4 V and 10 s at -1 V (versus Ag reference electrode). The post-annealed films showed zero electrical resistance at 60 K. The procedures for the fabrication of a high precision micro-sensor using YBCO superconductor for measurement of weak magnetic fields are outlined. The micro-sensor templates were patterned using X-rays and precursor films were deposited into the features.

INTRODUCTION

It has been demonstrated recently that electrodeposition can be used to fabricate high temperature superconductors [1-6]. This process has tremendous practical potential in the fabrication of planar and non-planar electronic devices and micro-sensors. Electrodeposition is a low-cost process and has the ability to deposit conductors or conductor-coated insulators of any shape. It is also an integral processing step in LIGA microfabrication, which involves lithography, electroforming and plastic molding. The short coherence lengths, anisotropy of electronic structures and low carrier densities of high-T_c oxide superconductors have not made them suitable for conventional superconducting electronic devices. However, these properties have been utilized to fabricate other devices such as magnetic field sensors. The abrupt increase in electrical resistance with the application of a weak magnetic field in high-T_c superconductors has been reported [7-8]. This property has been utilized in the fabrication of a bulk magnetoresistive sensor using YBCO superconductor by Nojima et al. [9]. These sensors were reported to exhibit a much higher sensitivity as compared with the traditional Hall Effect or semiconductor sensors and a magnetic field resolution of 2×10^{-6} G/(Hz) at 100 Hz in the 0.1 - 100 G range.

We are in the process of developing a microfabricated YBCO based superconductor microsensor for detection of weak magnetic fields. The LIGA process is being employed to achieve low cost, batch fabrication and integration with on-chip signal processing circuits. In this paper we report the electrochemical synthesis of YBCO thin film superconductors deposited from a single bath solution under pulsed plating conditions. Preliminary results of post-deposition annealing, T_c measurements, and electrodeposition into microfabricated template patterns will also be reported.

DISCLAIMER

EXPERIMENTAL

The precursors of YBCO superconductor were obtained by co-electrodeposition of the constituent metals using nitrate salts dissolved in dimethyl sulfoxide (DMSO). A typical electrolyte bath for YBCO films consisted of 0.07 M $Y(NO_3)_3 \cdot 5H_2O$, 0.180 M $Ba(NO_3)_2$, 0.07 M $Cu(NO_3)_2 \cdot 5H_2O$ and 0.003 M $Ag(NO_3)$ dissolved in 250 ml of (DMSO) solvent. All chemicals were of Analar or Puratronic grade and were used as received. A conventional three electrode cell was employed. The substrates (working electrode) were commercial-grade 0.125 mm thick Ag foils. The reference electrode was Ag (pseudo-reference) and the counter electrode was Pt gauze. Two opposed Pt gauze counter electrodes on either side of the working electrode were employed to deposit a stoichiometric film on both sides of the Ag substrate. A pulsed potentiostatic mode was employed to deposit the films and potential cycle was 10 s at -4.0 V followed by 10 s at -1.0 V. Film depositions were performed at room temperature with minimal stirring, thus assuring the process occurred in the diffusion-limited regime. A Princeton Applied Research potentiostat/galvanostat Model 273A with an IBM PC AT computer interface was used for controlling the pulsed-potential electrolysis and to monitor the current and voltage profiles.

A number of electrodeposition runs were conducted with different electrolyte compositions to optimize the composition of the as-deposited film. Inductively coupled plasma (ICP) spectrometry was used to analyze the composition of the electrolyte and the electrodeposited films. A ternary diagram showing how the electrolyte compositions were adjusted to reach the desired film composition is presented in Fig. 1. The films were annealed in air for 16 hours at 920° C. They were then annealed at 600° C for 4 hours and 400° C for 4 hours and very slowly cooled down to room temperature, while maintaining oxygen gas flow during these steps. X-ray diffraction analysis was carried out on the post-annealed films. The post-annealed film compositions were also measured using electron probe microanalysis (EPMA) and SEM images were taken to reveal the microstructure of the films. The superconducting transition temperature of the films was determined by the resistivity-temperature (R-T) measurement at a constant current in a four-point probe configuration.

RESULTS AND DISCUSSION

YBCO SYNTHESIS AND PROPERTIES

The electrolyte bath composition was optimized to produce YBCO precursor of the desired ratio. The composition of the optimized electrolyte bath as measured by ICP analysis was 0.077 M $Y(NO_3)_3 \cdot 5H_2O$, 0.184 M $Ba(NO_3)_2$, 0.072 M $Cu(NO_3)_2 \cdot 5H_2O$ and 0.003 M $Ag(NO_3)$ dissolved in 250 ml of (DMSO) solvent. The composition of the precursor films deposited from this bath (in terms of the ratio of the constituent elements Y/Ba/Cu) was 0.861/2.026/3.114. Ag content in the film was about 1% . A deposition rate of ~ 0.25 μm/minute was observed with the reported bath.

A series of samples was produced from the same bath with nearly the same composition each time and it showed that the electrodeposition process was very reproducible. DMSO was found to be an effective solvent to electrodeposit elements like yttrium and barium with very high negative reduction potentials. Interpreting the individual rate of co-deposition of the cations is very complex and depends on the mass transfer to the electrode, various surface effects, kinetic variables and the required overpotential. The most significant stand-alone parameter is the extra bias potential applied to the individual elements Y, Ba and Cu during the co-deposition process. The extra bias potential (the applied potential minus the reduction potential) for Cu is therefore

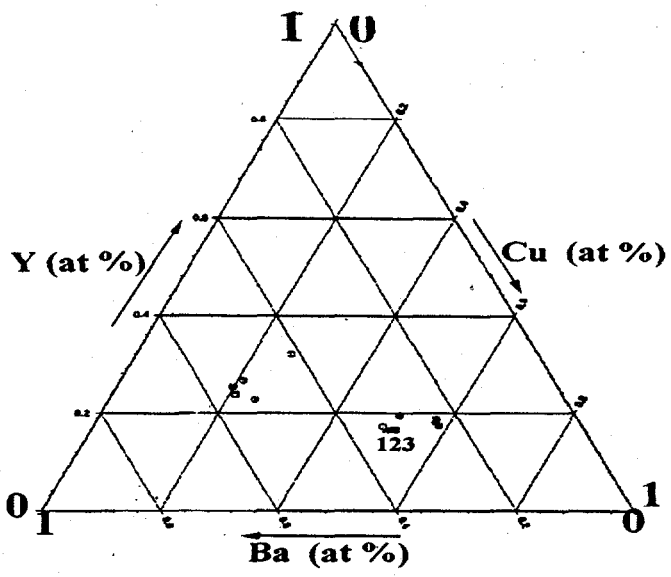

Figure 1. A ternary diagram showing the electrolyte composition map to the film composition. The deposition bath contains 3 mM $Ag(NO_3)$.

significantly higher than for Y or Ba. At -1.0 V, loosely bound materials are stripped off the substrate and Cu is deposited to maintain the conductivity of the deposited layer which then results in a significantly higher rate of deposition of Cu than Y or Ba. Addition of Ag during the deposition process as a co-deposited element was found to improve the uniformity of the deposit. Ag is believed to mitigate the weak-link problems associated with the superconducting films. Ag is also known to lower the melting point of all the oxide superconductors and influence the phase development and reaction process during the post -deposition annealing [10].

The X-ray diffraction pattern of the post-annealed film presented in Fig. 2 showed the c-axis textured orthorhombic superconducting $YBa_2Cu_3O_7$ phase. XRD peaks detected for Ag are from the substrate. The SEM of a post-annealed film is presented in Fig. 3. The resistivity - temperature (R-T) measurement was carried out in a four-point probe configuration and the superconducting transition is shown in Fig. 4. The post-annealed films showed reproducible zero resistance at about 60 K. The low value of the transition temperature (T_c) for this superconductor film suggests a low critical current density (J_c). However we believe this may not be detrimental to our intended application of fabricating a magnetoresistive sensor, where a suppression of the critical current in the film in its superconducting state at low magnetic fields is essential to exhibit a sharp jump in the resistance with the application of a weak magnetic field.

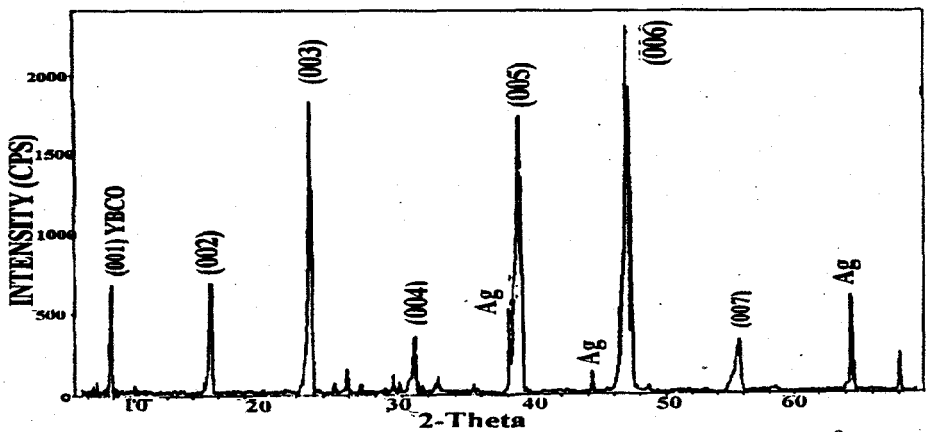

Figure 2. XRD spectra of an electrodeposited YBCO film on Ag annealed at 920° C for 16 hours.

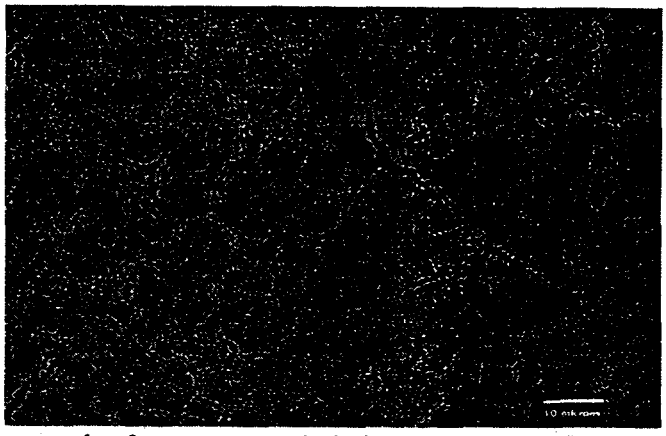

Figure 3. SEM micrograph of a post-annealed electrodeposited YBCO film on Ag substrate.

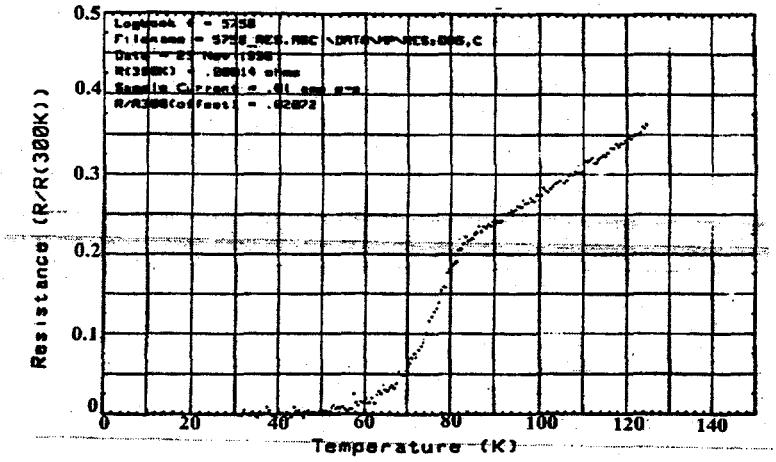

Figure 4. Resistance vs. temperature for electrodeposited YBCO films on Ag substrate.

Microsensor Device Fabrication

The schematic design of the magnetic field microsensor is illustrated in Fig. 5. The microsensor device fabrication sequence is presented in Fig. 6. In this sequence, an oxidized Si

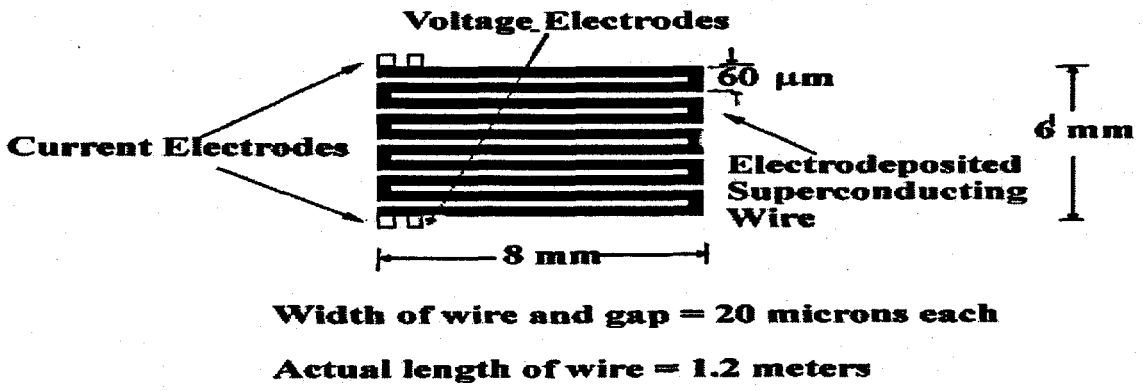

Figure 5. Schematic design of the microsensor. The meandered shape of the sensor is designed to increase its magnetoresistive sensitivity.

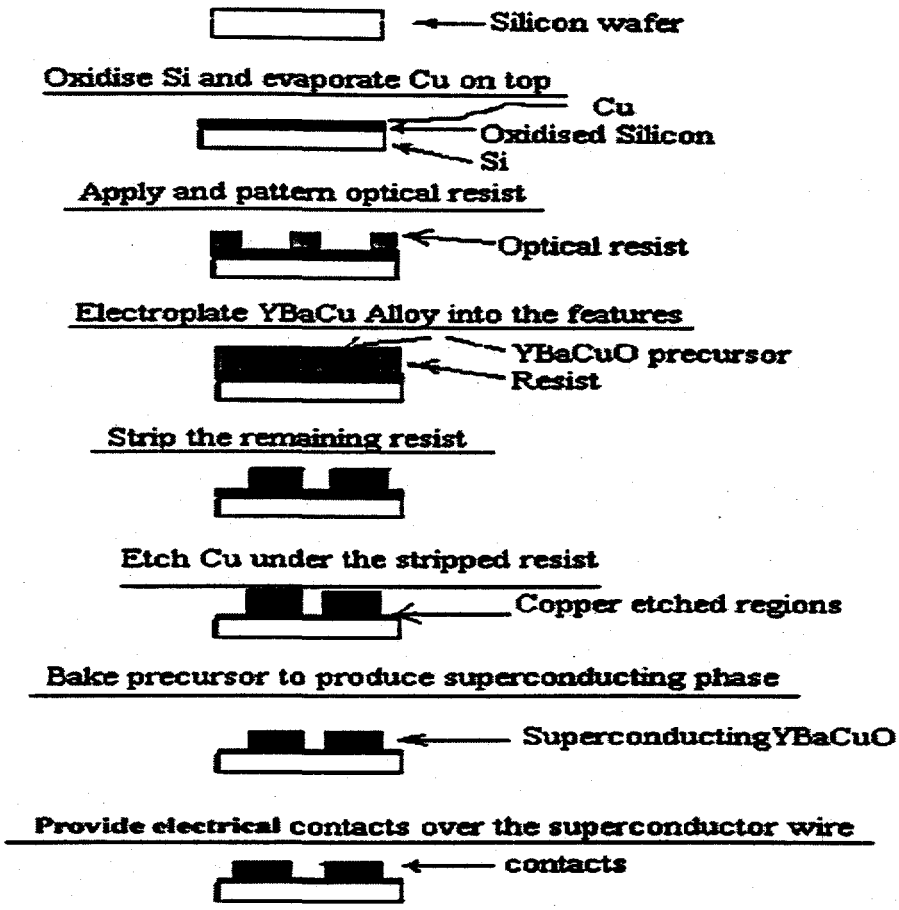

Figure 6. Fabrication sequence for the superconductor based microsensor

wafer is evaporated with a thin layer of 200A° of Cu or Ag as a plating base for depositing the YBCO precursor. Poly-methyl-methacrylate (PMMA), a positive photoresist, is spun coat onto the wafer to a thickness of about 3.0 μm. The resist is then patterned using X-rays, employing an X-ray mask, to produce the desired template. The patterned microsensor template is presented in Fig. 7. The patterns reveal well-defined features with the grooves and resist walls,

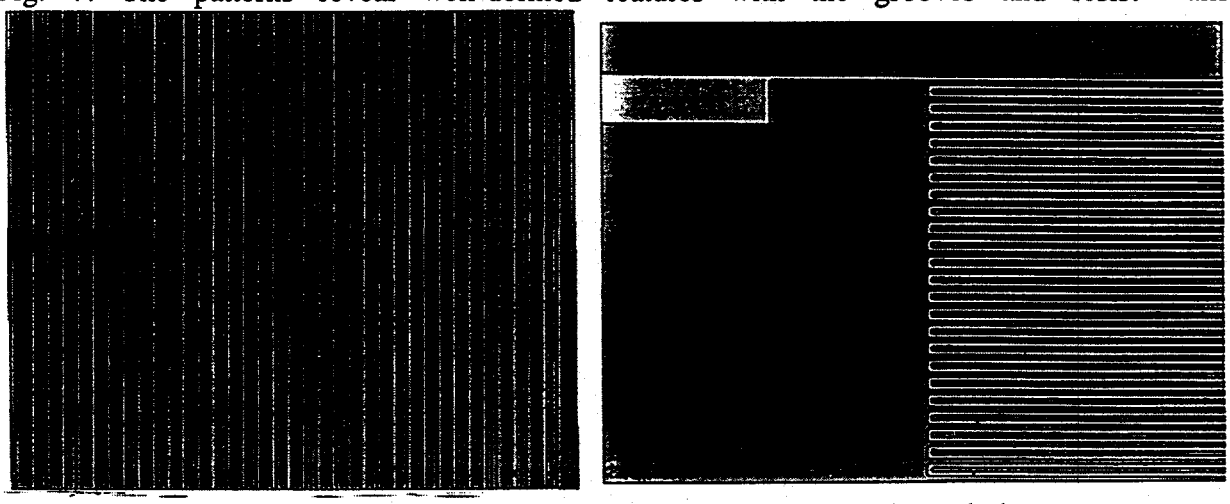

Figure 7. Patterned microsensor templates using an X-ray lithography technique.

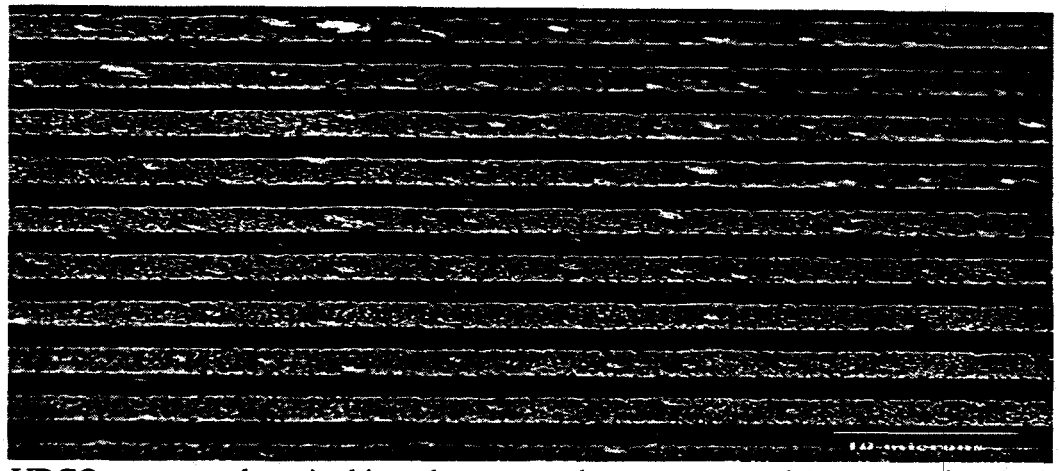

Figure 8. YBCO precursor deposited into the patterned grooves to produce a meandered wire.

each 10μm wide. The precursor films are subsequently electrodeposited into the patterned grooves to produce the meandered wire shape that is desired for our microsensor. An example is shown in Fig. 8. The composition of this precursor deposited into the patterns is being optimized. The effect of the Cu/Ag plating base and silica substrate on the superconducting properties of the post-annealed YBCO precursor is to be investigated and the sensor is to be calibrated for magnetoresistive applications.

CONCLUSIONS

We have electrodeposited YBCO precursor films with the desired elemental ratio on Ag substrates. Post-deposition annealing produced the orthorhombic superconducting $YBa_2Cu_3O_7$ phase. Resistivity - temperature measurements revealed superconducting behaviour with a T_c of 60 K. The fabrication of a weak magnetic field microsensor is being investigated. Preliminary results demonstrate the feasibility of electrodeposition as a processing technique in the fabrication of the sensor. The simplicity and low cost of the electrodeposition process, combined with the capability of batch fabricating microfeatures with superior geometry and functionality using the LIGA microfabrication technique, have the potential to open up a new realm in the field of microsystems technology.

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