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Studies on electrolytic deposition of Mg films and their oxidation

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Abstract : Preparation, characterisation and feasibility of polycrystalline MgO film substrates for superconducting films have been studied. The electrodeposition of magnesium subsequently followed by oxidation were carried out onto stainless steel substrates. Effect of heat treatment and other conditions have been discussed. White coloured MgO films are obtained which are compact, dense, uniform and adhesive to the substrates. On these MgO film substrate, we have screen printed the Bi–Sr–Ca–Cu–O ceramic and then tested for their feasibility in high-Tc superconductivity.

Keywords : Magnesium, electrodeposition, superconductivity

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Deposition of high quality films of the high-Tc superconductors onto different substrates has significant application in modern science and technology [1,2]. Among the different classes of possible substrate materials [3–5], the malleable and ductile substrates form an interesting class [6,7] since they offer hope for developement of replacement for wires, sheets and tapes, which have been difficult to realize due to brittle ceramic character of new high-Tc superconductors.

Uptill now, several research groups have prepared superconducting films onto single crystal substrates such as MgO, $SrTiO_3$, YSZ (Yttria stabilized Lirconia) *etc* [8–10]. However, for adaptability to large scale process, some inexpensive and easily available substrates are required. Some investigators prepared the superconducting films on polycrystalline MgO, YSZ pellets and stainless steel substrates [11–13]. Superconducting films have also been prepared by using SiO_2, ZrO_2 and indium-tin oxide as a buffer layer onto polycrystalline substrates [14–17].

In the present investigation, we have carried out the electrodeposition of Mg onto stainless steel, copper, brass and fluorine doped tin-oxide (FTO) coated glass substrates. The different preparative parameters of the deposition were studied and optimised. These as-deposited films were heat treated in order to obtain oxide film. White coloured MgO films are obtained which are compact, uniform and adhesive to the substrates. On the MgO film substrate, the Bi–Sr–Ca–CuO ceramic was screen printed and tested for temperature dependence of the resistivity at liquid nitrogen temperature.

Electrolytic bath was prepared by using reagent grade chloride of magnesium in double distilled water. Concentration of Mg-chloride was of 100 mM. The electrodeposition was carried out potentiostatically onto stainless steel, copper, brass and FTO coated glass substrates. The sheet resistance of conducting glass substrate was 20 to 30 ohm/cm. The back sides of the substrates were covered with insulating tape. The cathode area was one cm^2. The anode was a high purity graphite plate and distance between the anode and cathode was 0.6 cm. All depositions were carried out in an unstirred condition and at ambient temperature (300 K).

The cathodic polarization curves for solution of Mg chloride were recorded with the Scanning Potentiostat/galvanostat model 362 (EG & G) and X-Y recorder. Microstructural properties of the films were carried out with an Metzer optical microscope. Resistance of MgO film substrate was measured with eight and half digit 7081 precision voltmeter.

A microcomputer-controlled Philips PW 1710 X-ray diffractometer equipped with a copper target with CuK_α radiation was used to obtain the X-ray diffraction patterns of MgO film substrates.

Figure 1 shows the cathodic polarization curves of magnesium onto stainless steel, copper brass and FTO coated glass substrates. From these polarization curves, it is observed

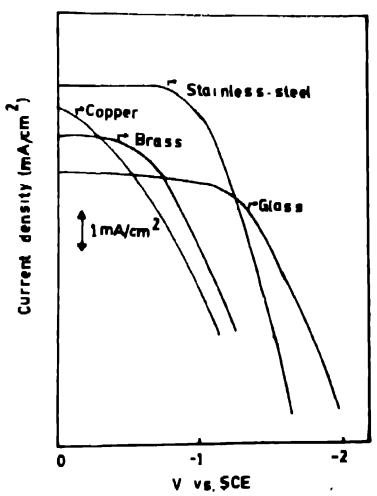


Figure 1. The cathodic polarisation curves for Mg onto different substrates.

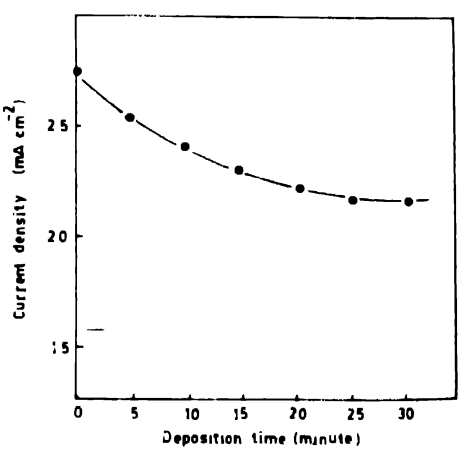


Figure 2. The variation of cathodic current density with deposition time

that nature of curves for Mg on copper and brass are similar and deposition occurs in the lower potential region. While the nature of curves for Mg on stainless steel and FTO coated glass substrates are very broad and diffuse in nature and deposition of magnesium occurs in the larger potential region. The values of set deposition potentials are optimised for all the substrates and are listed in Table 1.

Table 1. Electrodeposition potentials of magnesium from chloride solution onto different substrates

Substrate	Electrodeposition potential V *vs* SCE
Stainless steel	−1.20
Copper	−0.80
Brass	−0.90
FTO coated glass	−1.85

From Table 1, it is seen that set deposition potential of magnesium is smallest for copper and brass substrates, while for stainless steel and FTO coated glass substrates, large deposition potentials are required.

The films were deposited at constant potential and the variation of cathodic current density was recorded as a function of deposition time. For a given bath, the cathodic deposition current density was found to vary with deposition time. It is found that current density gradually decreases upto the deposition period of 25 minutes and then practically remained constant with deposition time. The current densities were found to lie between 2 to 4 mA/cm^2. Similar variations of current density with time was observed for all other substrates A typical curve is depicted in Figure 2.

The variation of thickness of the film was measured with deposition time for all substrates. A typical curve is shown in Figure 3. It was found in general, that the film

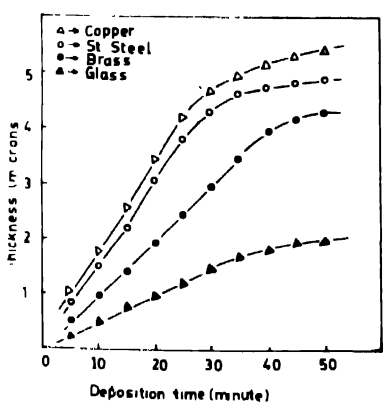


Figure 3. The variation of film thickness with deposition time.

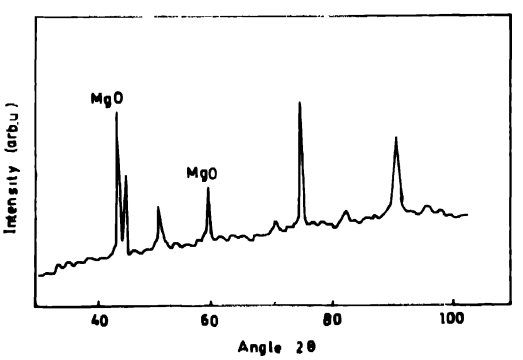


Figure 4. A typical X-ray diffraction pattern of MgO onto stainless steel substrate, oxidised at 400°C for five minutes

thickness gradually increases with deposition time and attains a certain value and then saturates for longer deposition times. The thickness of the film was found to lie between 2 to 4 microns for the deposition period of 50 minutes for different substrates.

These films are oxidised at 200°C to 400°C for five minutes, in order to obtain the complete oxidation of the films. Resistance measurements of as-deposited and oxidised films were carried out at room temperature by the precision 7081 voltmeter. From the resistance measurements, it is found that the resistance of as-deposited film is in the range of 4 to 6 megaohms, the resistance of the film increased on oxidation to around 20 megaohms.

From X-ray diffraction patterns, it is found that both as-deposited and oxidised Mg films are polycrystalline in nature; however, crystallinity improved after oxidation of the films. A typical X-ray diffraction pattern of MgO film onto stainless steel substrate, which was oxidised at 400°C for five minutes is shown in Figure 4.

Surface morphology of the as-deposited and oxidised Mg films were studied Figures 5(a, b) show the typical microphotographs of as-deposited and oxidised Mg films with magnification 500 X. White coloured deposits are obtained which are dense, uniform and adhesive to the substrates. The as-deposited film consists of packed arrangement of grains, while grain size of the oxidised films was increased with increase in oxidation temperature.

The Bi–Sr–Ca–CuO ceramics were screen-printed onto MgO film substrates and then heated in oxygen atmosphere at 1100 K for 10 minutes. The films turned into dark black in appearance, adhesive to substrate and stable towards atmospheric conditions. These substrates are as good as single crystal substrates. Figure 6 shows the resistivity dependence of temperature of screen printed BSCCO film.

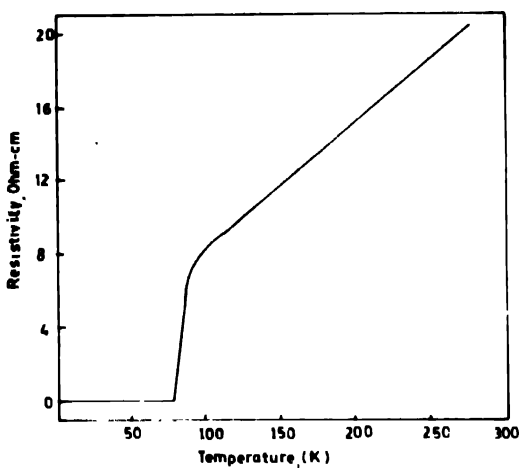
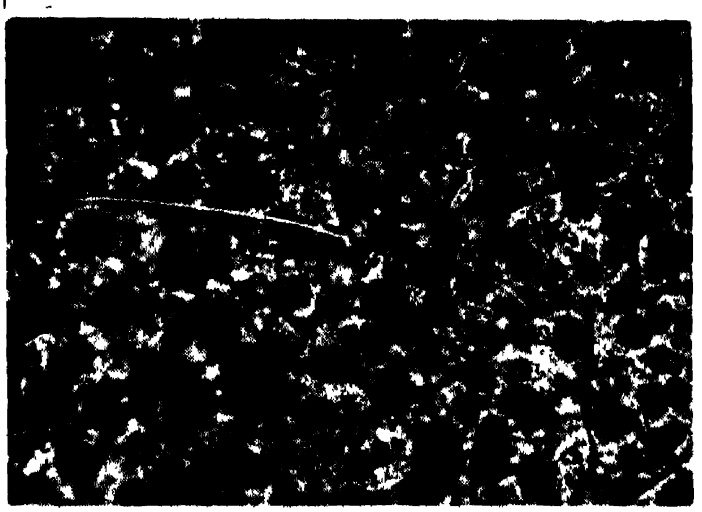


Figure 6. Resistivity dependence of temperature of screen printed BSCCO film

The resistivity measurement was done using a four probe method with a silver paint contacts on the film surface. It is found that the resistivity of the film was in the range

Plate I

(a)



(b)

Figure 5. Microphotographs of MgO films with magnification 500 X (a) as deposited, (b) oxidised at 400°C.

of 15 to 20 ohm/cm at room temperature and found to decrease drastically at liquid nitrogen temperature.

In this work, electrodeposition of Mg films are carried out onto stainless steel, copper, brass and FTO coated conducting glass substrates. Oxidation of the film is necessary in order to obtain the pure oxidised film of MgO. X-ray diffraction patterns show the MgO films are polycrystalline in nature. The MgO films onto stainless steel substrate are used as a barrier layer for obtaining high-Tc superconducting films.

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