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Formation of oxidation-resistant Cu-Mg coatings on (001) Cu for oxide superconducting tapes

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ABSTRACT

The formation of oxidation-resistant buffer layers on (001) oriented Cu for coated high-temperature superconducting tape applications was investigated. The approach employed Cu/Mg multilayer precursor films that were subsequently annealed to form either Mg-doped fcc Cu or intermetallic Cu_2 Mg. The precursor consisted of an Mg/Cu multilayer stack with 5 each of 25 nm thick Mg and 25 nm thick Cu layers which were grown at room temperature by sputter deposition. At annealing temperature of 400 °C, formation of the intermetallic Cu_2 Mg was observed. X-ray diffraction showed that the Cu_2 Mg (100) oriented grains were epitaxial with respect to the underlying Cu film, possessing a cube-on-cube orientation. In order to test oxidation resistance, CeO_2 films were deposited at elevated temperature on Ni/(Cu,Mg)/Cu/MgO structures. In case of the CeO_2 film on Ni/Cu/MgO, significant surface roughness due to the metal oxidation is observed. In contrast, no surface roughness is observed in the SEM images for the CeO_2/Ni/(Cu,Mg)/Cu/MgO structure.

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1. Introduction

Contemporary approaches to realizing long-length high-temperature superconducting (HTS) tape involve the deposition of superconducting oxide films on metal tapes [1,2]. In one approach, known as Rolling Assisted Biaxially-Textured Substrates (RABiTS), epitaxial superconducting thin-film oxides are grown on biaxially-textured metal tapes [3–9]. The crystallographic texture in the metal tape is translated into the superconductor through epitaxial growth of applicable buffer layers and superconducting films [10]. The highly-aligned, crystallographic texture eliminates the detrimental effects of large-angle grain boundaries that suppress the superconducting critical current in superconducting cuprate thin films [11,12], an effect that is characteristic of the cuprates but not observed in non-oxide superconductors [13]. For the RABiTS approach, the base metal substrate materials that have been explored to date include Ni alloys [14], Ag [15], and Cu [16]. Interest in copper as the base metal primarily stems from three factors. First, the {100}<100> crystallographic cube texture that can be achieved in copper by cold-rolling followed by annealing is quite sharp. Second, in a practical superconducting tape application, a mechanism for shunting of the conductor current will be needed in order to protect against failure of the superconducting film [17]. The high normal state conductivity of copper makes it attractive for this function. Third, the inherent ferromagnetism in many Ni alloys introduces hysteretic losses in AC applications [18]. The use of diamagnetic Cu circumvents this limitation.

A significant issue with the use of Cu tapes for high temperature superconductor (HTS) coated conductors is the oxidation of the metal substrate during buffer oxide and $YBa_2Cu_3O_7$ deposition. The epitaxial growth of these oxides occurs at elevated temperature in a background of oxygen gas. In general, the oxidation of Cu proceeds rapidly and at minimal oxygen partial pressure. Copper oxide (Cu_2O, CuO) growth occurs at the oxide-gas interface; the rate-determining step in Cu oxidation is the diffusion of cation vacancies [19]. In the temperature range (300–800°C) that is typical for epitaxial deposition of oxides, Cu_2O formation is favored. Copper oxide is stable at high temperatures for oxygen pressures as low as 10^{-8} Torr. Copper oxide is not an effective passivation layer to further oxidation or scaling. A typical RABiTS structure is composed of oxide buffer layers, such as CeO_2, Y_2O_3 and yttria-stabilized zirconia (YSZ) at the metal interface [20–22]. At the temperatures necessary for $YBa_2Cu_3O_7$ epitaxy, these

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oxides will not block oxygen diffusion, resulting in the oxidation of Cu substrate.

In the use of copper for metallurgical applications, enhancement of Cu oxidation resistance has been pursued by several approaches, including alloying or implanting elements, such as Mg, Cr and Al, that are known to be oxygen getters [23–29]. In the electronics area where oxidation of copper interconnects is an issue, Mg-doped Cu films have been investigated as oxygen diffusion barriers [30]. The phase diagram for the Cu-Mg binary alloy system indicates limited Mg solubility in fcc Cu; an intermetallic compound, Cu_2 Mg, is observed at the Mg composition range of range of 15–18 weight % [31]. Interestingly, the crystal structure of Cu_2 Mg is cubic fcc with the lattice constant a = 7.064 Å [32]. The room temperature resistivity of Cu_2 Mg is 5–6 μΩ-cm, which is comparable with that of Cu (1.67 μΩcm) [33].

In this work, the formation of (Cu,Mg) films on a (001) Cu surface is investigated, focusing on the applicability of these layers as oxidation resistant buffers for Cu-based RABiTS HTS conductors. The (Cu,Mg) provides a barrier to oxygen diffusion into the Cu base substrate by first acting as an oxygen getter, eventually forming an MgO diffusion barrier. In engineering a Cu tape with useful resistance to oxidation, one can consider two variants of (Mg,Cu) buffer layers for Cu substrates, namely Mg-doped fcc Cu and the cubic Cu_2 Mg intermetallic.

2. Experimental description

The substrates employed for these experiments were epitaxial (001) Cu films on (001) MgO single crystals. The Cu films were grown using sputter deposition at a substrate temperature of 400 °C. The Ar gas pressure used for sputter deposition was 1.33×10^{-5} bar. The thickness of the epitaxial Cu films was 180 nm. Due to the high vapor pressure of Mg (over 2.67×10^{-6} bar at 400 °C), in situ growth of epitaxial (Cu,Mg) films is difficult. The approach used in this study was to deposit Cu/Mg multilayer precursor films on the (001) Cu/MgO substrates at room temperature. The multilayers were then annealed to form either Mg-doped fcc Cu or intermetallic Cu_2 Mg. Sputter deposition was used to deposit Mg and Cu multilayers at room temperature with 1.33×10^{-5} bar of Ar gas. The precursor multilayer consisted of an Mg/Cu multilayer stack with 5 each of 25 nm thick Mg and 25 nm thick Cu layers. Fig. 1 shows the vertical structure that was used for this study. This precursor was then annealed for 1 hr in a tube furnace in a flowing 4% H_2/96%Ar (reducing) mixture at temperatures ranging from 400 °C to 700 °C. X-ray diffraction was employed to track (Cu,Mg) phase formation as the multilayer was subjected to various annealing temperatures and durations. For growth and annealing experiments, the heating and cooling rates were approximately 10°C/min. Sample dimensions were either 0.5 × 0.5 cm or 1 × 1 cm. The study did not include any cross-section scanning electron or transmission electron microscopy to confirm the presence of the CuMg layers. However, the deposition of the Cu/Mg was confirmed by simultaneous deposition on oxide substrates (e.g. $SrTiO_3$) on which the deposition thickness was calibrated. Obviously, there will be diffusion of the coating with the Cu layer. The presence of the Cu-Mg intermetallic also confirms the presence of Mg in the deposited film.

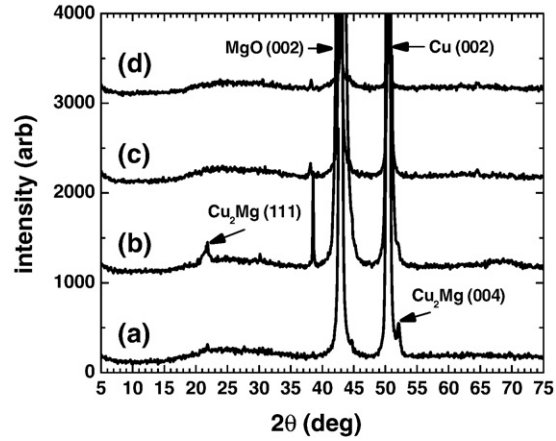

Fig. 2. X-ray diffraction scan for Mg/Cu multilayer structures on (001) Cu/MgO, annealed at (a) 400 °C, (b) 500 °C, (c) 600 °C, (d) 700 °C.

3. Results and discussion

Fig. 2 shows θ–2θ x-ray diffraction scans of (Cu,Mg) multilayers after annealing at 400, 500, 600, and 700 °C for 1 hr. At the upper end of the temperature range (600 °C, 700 °C), only the (00 L) Cu peaks are observed. This is consistent with the formation of an epitaxial Mg-doped fcc Cu alloy. In contrast, annealing the multilayer structure at a temperature of 400–500 °C resulted in the formation of the intermetallic Cu_2 Mg on the Cu surface. The impurity peak at approximately 38° could correspond to MgO (111). Fig. 3 shows a θ–2θ X-ray diffraction scan along the surface normal for a multilayer structure annealed at 400 °C. The dominant diffraction peaks were from the (00 l) MgO substrate, (00 l) Cu film, and Cu_2 Mg. Both (111) and (001) oriented Cu_2 Mg grains are observed. The relative intensities for the (111) and (001) Cu_2 Mg peaks varied somewhat between samples but we prominent only for annealing temperatures of 400 and 500°C. Note that Fig. 2 is a linear

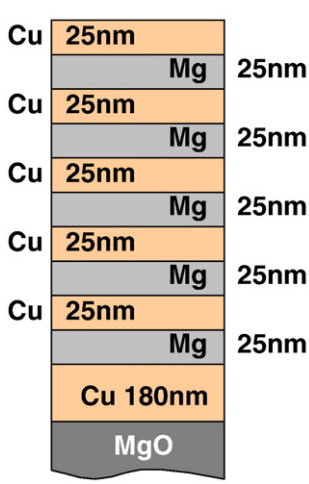

Fig. 1. The vertical multilayer Cu/Mg precursor structure that was employed.

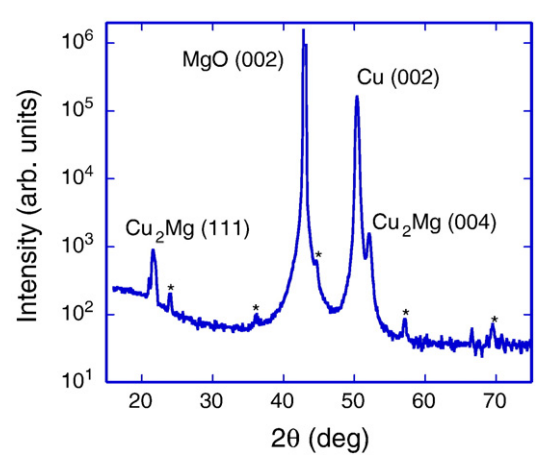

Fig. 3. X-ray diffraction scan for a Mg/Cu multilayer structure on a crystalline (001) Cu/MgO substrate, annealed at 400°C, showing the formation of Cu_2 Mg. The peaks marked by asterisk appear to correspond to polycrystalline copper oxide or magnesium oxide.

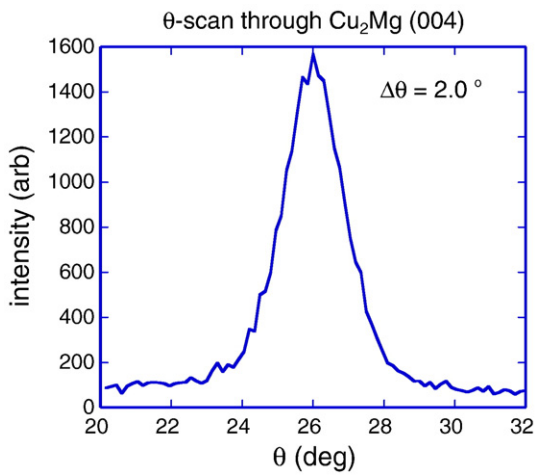

Fig. 4. Rocking curve of the Cu_2 Mg (004) diffraction peak for the sample annealed at 400°C.

intensity plot, while Fig. 3 is a log intensity plot. Interestingly, the (001) oriented component of the intermetallic phase was found to be epitaxial with respect to the Cu layer. Fig. 4 shows the x-ray diffraction rocking curve for the (004) Cu_2 Mg peak. The full-width half-maximum (FWHM) of the Cu_2 Mg (004) is $\Delta\theta = 2.0°$, which is only slightly larger than that for the Cu film ($\Delta\theta = 1.45°$). The in-plane orientation of the c-axis oriented Cu_2 Mg was investigated using four-circle x-ray diffraction. Fig. 5 shows an in-plane φ-scan through the Cu_2 Mg {222}. The four-fold symmetric peaks indicate that the grains are epitaxial with respect to the Cu film, possessing a cube-on-cube orientation. The FWHM of the in-plane peaks is 2.1°. The cubic Cu_2 Mg out-of-plane lattice parameter was measured to be 7.016 ± 0.005 Å. The epitaxial relationship of the Cu_2 Mg is cube-on-cube with an out of plane relationship of Cu_2 Mg(001) || Cu(001) || MgO(001), and an in-plane relationship of Cu_2 Mg(100) || Cu(100) || MgO(100). The cube-on-cube texture of the Cu_2 Mg is potentially useful as a crystalline template for (001) oriented epitaxy of subsequent buffer layers with cubic or tetragonal crystal structure.

In order to assess the oxidation resistance of the structures possessing (Cu,Mg) alloy films relative to its application in coated HTS conductors, a CeO_2 film was deposited at elevated temperatures on Ni/(Cu,Mg)/Cu/MgO substrates and compared to CeO_2 films on Ni/Cu/MgO. The 300 nm thick Ni layer was added to the substrate structures

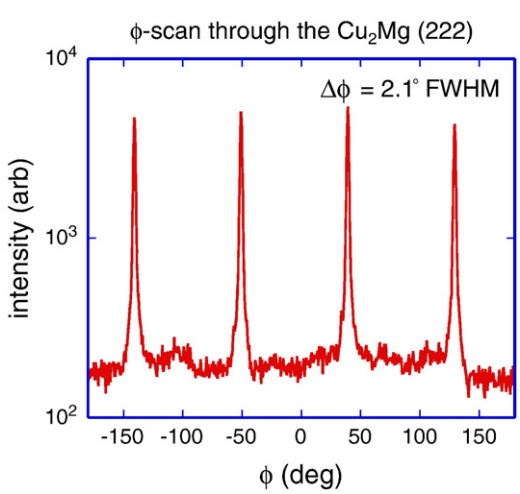

Fig. 5. In-plane φ-scan through the Cu_2 Mg {222} peak showing cube-on-cube in-plane epitaxy with the (001) Cu film.

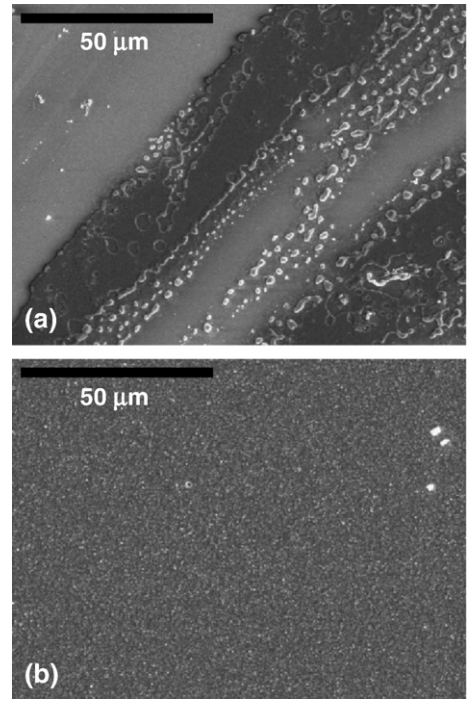

Fig. 6. Scanning electron microscopy image showing the surface morphology after CeO_2 deposition on (a) Ni/Cu/MgO and (b) Ni/(Cu,Mg)/Cu/MgO, indicating the oxidation resistance of the (Cu,Mg) coating.

since the behavior of the CeO_2/Ni interface is relatively well understood from previous HTS coated conductor studies. It should be noted that the addition of the Ni layer will also decrease the susceptibility of the surface to oxidize, given that Ni is more resistant to oxidation than is Cu. The CeO_2 films were deposited by pulsed laser deposition at a substrate temperature of 750 °C. The CeO_2 deposition sequence included a thin CeO_2 nucleation layer deposited in vacuum, followed by CeO_2 deposition at 2.67×10^{-7} bar of oxygen. In the case of the CeO_2 film on Ni/Cu/MgO, significant roughening of the surface was observed due to oxidation of the Cu. This is shown in the SEM image in Figure 6ss The observed particles on the surface include copper oxide and nickel oxide. In contrast, the surface for the CeO_2/Ni/(Cu,Mg)/Cu/MgO structure remained remarkably smooth. The resistivity of Cu increases with Mg dopant concentration. This may be an important factor if supercurrent shunting through the substrate is expected. For the conditions considered, the CeO_2 film was not epitaxial with respect to the Cu-Mg surface. Future studies should address the nucleation of epitaxial oxides on the Cu-Mg cubic surface. Fundamental studies have shown that the orientation of epitaxial oxides grown on metals depends on both the surface termination [34] and miscut orientation [35]. These issues will need to be addressed for the Cu-Mg fcc alloy or Cu_2 Mg intermetallic surface. Ideally, the oxide buffer employed should also be conducting[36,37], thus allowing the possible shunting of current directly through the buffer into the Cu tape.

4. Conclusion

We have investigated the formation of Cu-Mg coatings on (001) Cu as an oxidation barrier. The targeted application is oxidation-resistant biaxially-textured Cu for high-temperature superconducting coated conductors. High-temperature superconducting biaxially-textured coated conductors hold significant promise for the development of a superconducting tape technology functional at liquid nitrogen temperatures. The use of high conductivity, oxidation-resistant Cu tapes may addresses the issues of substrate ferromagnetism and supercurrent

shunting. High temperature annealing of Mg/Cu multilayers on (001) Cu resulted in oxidation-resistant Mg-doped (001) Cu. Moderate temperature annealing yielded the intermetallic Cu_2 Mg. Epitaxy of (004) Cu_2 Mg intermetallic phase was achieved on the (002) Cu film. X-ray diffraction θ-2θ scans, Δθ rocking curves, and in-plane φ-scans through the Cu_2 Mg (222) indicate that the (001) oriented component of the Cu_2 Mg phase is epitaxial with respect to the (001) Cu. The progression from Cu_2 Mg to Mg-doped Cu with annealing temperature reflects a kinetic progression of Mg diffusion in the Cu matrix. Given its stability at elevated temperature, the Mg-doped fcc Cu phase is the most attractive as a viable oxidation-resistant buffer.

Acknowledgements

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