Enhanced J_c's of $YBa_2Cu_3O_{7-x}$–Ag *ex situ* annealed coevaporated films on $LaAlO_3$ (100) substrates

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A 5× increase of the critical current density (J_c) at 77 K was obtained by coating a coevaporated 500 nm thick Y, BaF_2, Cu film with 50 nm Ag prior to the *ex situ* annealing. J_c increased from 0.2 for uncoated samples to 1 MA/cm^2 for the Ag-coated sample without severely affecting the zero resistance transition temperature (T_{c0}). Scanning electron microscopy showed that the surface morphology was improved and that the normally observed trellislike structure was greatly reduced. By combining electron microscopy and sputter assisted Auger analysis it was found that the Ag nucleated in droplets on the surface of the superconductor with only small amounts of Ag in the superconductor matrix. X-ray diffraction confirmed that the Ag-coated film was highly *c*-axis oriented. The increase in J_c is believed to be due to the improved surface properties of the superconductor, indicating that a larger amount of the film is *c*-axis oriented or that the single-crystalline grains are larger. © *1994 American Institute of Physics.*

The BaF_2 coevaporation technique in combination with optimized *ex situ* annealing at low oxygen partial pressures is commonly used for fabrication of high-temperature superconducting thin films with good transport properties.[1–3] Films fabricated using this process have also shown good microwave properties.[2] However, the critical current density (J_c) decreases as the film thickness is increased.[3] This limits the usefulness of the process in comparison with other techniques such as the laser ablation process. A compensation for the decrease in J_c is therefore necessary. Recent work has shown that incorporation of silver (Ag) into $YBa_2Cu_3O_{7-x}$ (YBCO) superconducting material enhances J_c.[4–6] This has resulted in J_c's in the excess of 1 MA/cm^2 in films produced by laser ablation[4] and by the dipping-pyrolysis process.[6] The higher values of J_c in the Ag doped films are postulated to be due to two effects: (i) the contact resistance between the superconducting grains are reduced and (ii) a larger amount of the YBCO film is *c*-axis oriented.[6] In this letter we study the superconducting properties obtained by adding Ag to 500 nm thick YBCO films prepared by the BaF_2 coevaporation technique. The film coated with Ag prior to the annealing step showed a significant improvement in J_c and in the degree of crystallinity compared to uncoated films.

The films were deposited by coevaporation of Y (99.999%), BaF_2 (99.99%), and Cu (99.99%) onto (100) $LaAlO_3$ substrates in a VG UHV chamber with a base pressure of less than 10^{-9} Torr. Ag (99.999%) was deposited by thermal evaporation from Mo boats. *Ex situ* annealing was performed in a quartz tube furnace in a two-step optimized annealing procedure. The first step is a 1 h annealing at 800 °C in a total Ar–O_2 mixture flow of 1000 sccm [$p(O_2)$=100 Pa] bubbled through de-ionized H_2O. The second step is a 1 h annealing at 525 °C in 1 atm dry oxygen with a flow rate of 200 sccm. The measurement of the zero resistance transition temperature (T_{c0}) was done using a standard four-point probe technique. The measurement of J_c at 77 K was done using a contactless, inductive measurement technique.[7] All quoted values of J_c are measured with no magnetic field applied.

Scanning electron microscopy (SEM) for near-surface imaging of the YBCO films was performed using a Phillips XL20 instrument equipped with an energy dispersive x-ray analysis (EDAX) facility. Phase identification was done with x-ray diffraction (XRD) using a Phillips PW 1710 Θ-2Θ diffractometer with diverging slits. A PHI 590A scanning Auger microprobe with a base pressure of less than 2×10^{-10} Torr, combined with *in situ* argon-ion milling, was used to study the compositional properties of the YBCO–Ag film. The Auger spectra were obtained with a 10 keV primary beam. The Ar^+ sputtering ion energy was 2 keV and the fluency was 25 μA cm^{-2}.

The results of the T_{c0} and the J_c measurements plotted against the nominal film thickness for uncoated films are shown in Fig. 1. As can be seen from this figure, the T_{c0} values increase as the nominal film thickness increases, but the J_c values decrease with increasing nominal film thickness. The J_c values for films with a thickness less than 300 nm are above 1 MA/cm^2, but for thicker films J_c values are significantly lower than 1 MA/cm^2. However, with Ag de-

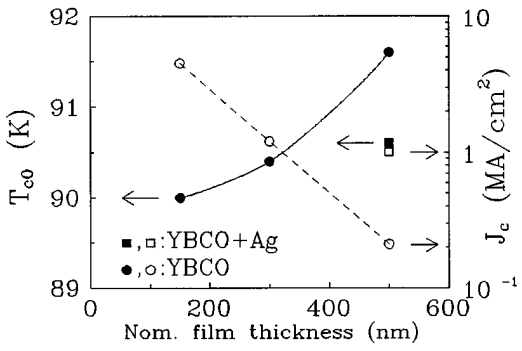

FIG. 1. Zero resistance transition temperature T_{c0} and critical density J_c (77 K) vs nominal YBCO film thickness.

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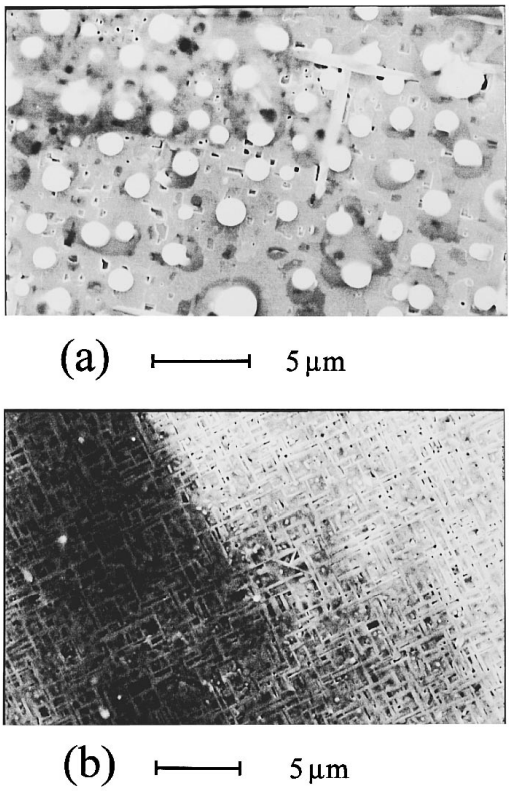

FIG. 2. SEM pictures of (a) coevaporated Y, BaF_2, Cu film coated with Ag prior to the annealing and (b) uncoated, coevaporated Y, BaF_2, Cu reference film. Film thicknesses for both samples are 500 nm. Note the different scales.

posited on top of the 500 nm thick films prior to the annealing, it is possible to compensate for this decrease in J_c. From Fig. 1 it can be seen that this treatment enhances the value of J_c with a factor of 1 to 5 MA/cm^2 for films with 500 nm nominal thickness. With Ag in the YBCO film T_{c0} is lowered by approximately 1 K for films with 500 nm nominal film thickness, but the transition width (<1 K) remains the same as for the uncoated films.

Figure 2 shows SEM pictures of a reference YBCO film and the Ag-coated YBCO film. The reference sample was fabricated with the same thickness and under similar conditions as the Ag-coated film, but without coating with Ag. The Ag-coated film [Fig. 2(a)] shows a significant improvement of the surface morphology in that the commonly observed trellislike structure on the reference sample [Fig. 2(b)] is greatly reduced. However, spherical droplets have nucleated on top of the surface [Fig. 2(a)]. Using EDAX we found that there was less than 2 at. % Ag in the YBCO film implying that practically all the Ag have nucleated in the spherical droplets. The improvement in J_c is in part believed to be due to the improved surface morphology. The x-ray-diffraction pattern of the Ag-coated YBCO film (Fig. 3) shows a preferential c-axis (001) orientation in the superconducting film with very low yields from any of the a- ($h00$) and b-axis ($0k0$) planes. This is also in accordance with the measured high J_c value.

Auger analysis was performed both between the Ag droplets (Fig. 4) and on different Ag droplets. From Fig. 4 it

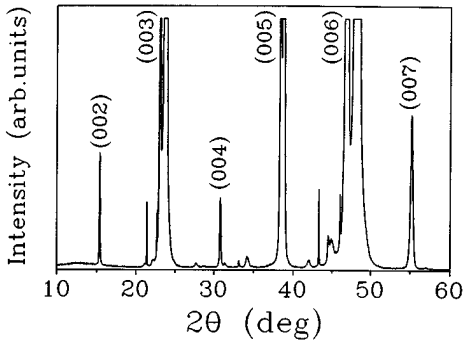

FIG. 3. X-ray-diffraction pattern of the coevaporated Y, BaF_2, Cu 500 nm thick film coated with Ag prior to the annealing. $LaAlO_3$ substrate reflections overlap both (003) and (006) YBCO reflections. Cu reflections are identified at $2\Theta \approx 21.5°$ and 43°.

is seen that there is a very low amount of Ag in the superconducting matrix in accordance with our EDAX measurements, and that the distribution of elements in the film are homogeneous. The Auger analysis on the Ag droplets showed a high concentration of Ag in the near-surface region, and that the distribution of elements were not homogeneous throughout the film.

Our results show that the BaF_2 process can be used to fabricate superconducting thin films with properties comparable to other thin-film deposition processes.[4,6] The reason for the enhancement of J_c is believed to be due to the improved properties of the Ag-coated films as compared to uncoated films, i.e., improved surface morphology, crystallinity, and element distribution in the films. However, Ag droplets are present at the surface of the superconductor, and their presence might limit the usefulness of the films in device applications. To avoid Ag to nucleate on the surface of the film, a smaller amount of Ag could perhaps be deposited on top of the film or Ag could be coevaporated along with the three other elements.

Preliminary results for coating coevaporated 500 nm thick Y, BaF_2, Cu films with other group-IIB elements (i.e., Cu and Au) prior to the annealing shows an order-of-magnitude drop in J_c for coating with Cu. However, coating

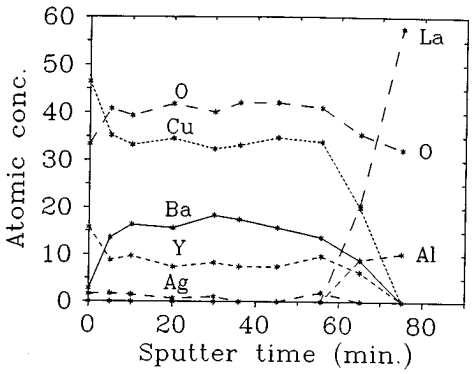

FIG. 4. Sputter Auger profiles for 500 nm thick YBCO film coated with Ag prior to the annealing. The Auger electron probe (10 keV) was focused between the Ag drops. Reliable sputter profiles were difficult to obtain from the $LaAlO_3$ substrate due to charge pileup.

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with Au J_c increases to 0.8 MA/cm^2. SEM pictures of the Au-coated film show the same reduction in the trellislike structures with spherical droplets nucleating on the surface of the film as was the case for the Ag-coated film.

In summary, we have shown that the BaF_2 process combined with thermal evaporation of Ag before the two-step annealing can be used to fabricate 500 nm thick superconducting films with J_c values above 1 MA/cm^2 and T_{c0} values above 90 K. The films were highly c-axis oriented with a good surface morphology, as deduced from XRD and SEM analysis.

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