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HIGH CRITICAL CURRENT DENSITIES IN Nb_3Sn FILMS WITH ENGINEERED MICROSTRUCTURES -- ARTIFICIAL PINNING MICROSTRUCTURES

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ABSTRACT

Films with layers of Nb, Cu, and Sn have been fabricated to simulate a Nb_3Sn bronze-type process. These Nb_3Sn films have produced critical current densities greater than 1 x 10^6 A/cm^2 at 4.2 K and 7.5 T. Niobium films doped with Y, Sc, Dy, Al_2O_3, and Ti have been deposited with e-beam co-evaporation onto 75 mm diameter Si wafers with a 100 nm SiO_2 buffer layer. The Nb layer was followed by a layer of Cu and a layer of Sn to complete the bronze-type process. The films with the highest J_c had about 8 vol. % Sc and about 18 vol. % Al_2O_3. Characterization of the microstructure by TEM shows that these high J_c films contained high density of inclusions about 5 nm in size and that the grain size of the Nb_3Sn is about 20-25 nm for samples heat treated at 700°C for up to eight hours.

INTRODUCTION

To increase the critical current of Nb_3Sn the microstructure and composition must be controlled on a nanometer scale. One would like to "engineer the microstructure" (EM) to have small grains with the optimum composition. To engineer the microstructure in "bronze-type" processes one must add elements that do not alloy with Nb or Cu but form oxides or intermetallics with Cu or Sn.[1,2,3,4] This would make most of the rare earth elements candidates (i.e. lanthanide period) plus elements of the second and third groups (i.e. Y and La). These elements readily form oxides but also form many intermetallics with

Cu and Sn. To enhance the H_{c2} of the films and to determine if there is any interaction with other dopants Ti was also investigated. To test the engineered microstructure concept for bronze-type conductors the additions must have a very low solubility in Nb and should co-deform well with Nb. The later condition does not have to be met at this time since a thin film approach has been taken to achieve a fine distribution of the addition in the Nb. Once perfected the film technique should permit the rapid screening of candidate elements. It should also produce a uniform fine scale distribution of the addition in the film prior to heat treatment which should act as artificial pinning centers once the compounds are formed.

THIN FILM APPROACH

This work intends to first identify elements that can increase the critical current of Nb_3Sn by using thin film processing techniques. This permits one to separate fabrication issues, i.e. filament non-uniformity, from the fundamental superconducting materials issues, i.e. grain size and composition, that affect critical current. The wire fabrication issues associated with a new wire processing method will be addressed later.

Thin films of (Nb-X)-(Cu-Sn) are produced by e-beam co-evaporation onto Si substrates with an SiO_2 buffer layer. Figure 1 shows a schematic of the as-deposited film in cross section. With the addition of certain elements (mostly rare earth elements which do not alloy with Nb) to the Nb film, one can produce a uniform dopant distribution in the Nb on a nanometer scale prior to heat treatment. The initial elements chosen to add to the films to test the EM approach were Y, La, Sc, Dy, and Ti. The Ti has been added to increase the upper critical field (H_{c2}). Ultimately the films will be doped with at least two elements such as Y or Dy and Ti; one to alter the microstructure and the other to enhance H_{c2}. This is also necessary to determine if there are any Y and Ti interaction or compound formation. After heat treatment and patterning for I_c measurements one obtains the structures seen in figs. 2a, 2b, and 3.

SAMPLE FABRICATION

Using physical vapor deposition techniques (e-beam, sputtering and evaporation) films were prepared with the layer sequence of Nb, Cu, and Sn with thicknesses of about 200 to 400 nm. After the films have been heat treated to produce Nb_3Sn they are patterned using photolithography and etching techniques to produce lines and voltage and current pads for critical current testing.

Additions of Ti, Dy, Y, Sc, La, and Al_2O_3 were incorporated in the Nb layer by e-beam co-evaporation. Since Sn is not permitted in the e-beam deposition system used for this work and must be applied with another system a Cu layer about 400 nm thick is added to prevent oxidation of the Nb layer before the films are removed from the e-beam chamber. The e-beam system permitted the co-deposition of up to three elements simultaneously. The Nb and Cu deposition rates were kept as close to 4.0 Å/s as possible. The deposition rate for Ti, La, and Y was about 0.1-0.2 Å/s to produce a composition of about 5 volume percent of each addition. This could be higher or lower depending on the sample. The base

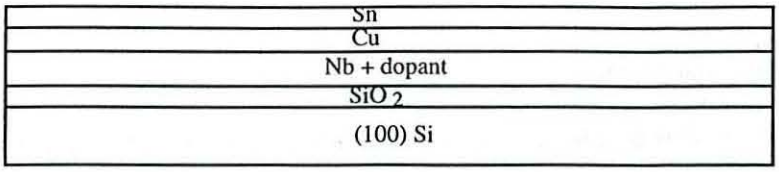


Fig. 1 Schematic of as-deposited film in cross section on (100) Si substrate with an SiO_2 buffer layer.

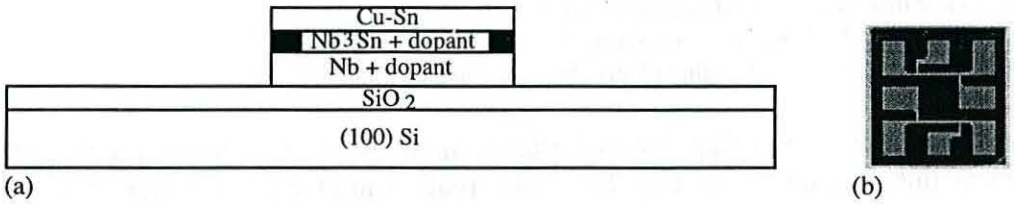


Fig. 2 (a) Schematic of the film in cross section after heat treatment and patterning using standard photo-lithography techniques developed for semiconductor processing to produce lines and voltage and current pads for critical current measurements. (b) A photograph of a patterned chip (15 x 15 mm^2). Each chip has two lines 250 μm wide and a total Nb plus Nb_3Sn thickness of about 400-500 nm.

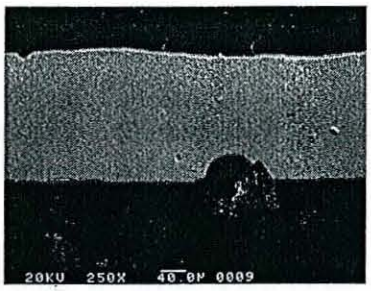


Fig. 3 Scanning electron microscope image of a line from an undoped film heat treated for 60 minutes at 700°C. Note the defect in the line that was introduced during photolithography.

pressure for the system was usually 3 x 10^{-7} Torr. With such a high base pressure it is possible that some oxygen was incorporated into the Nb alloy layer during deposition.

A Sn layer about 200 nm thick is then applied by either sputtering or evaporation. The wafer processing is listed in Table I. By monitoring the deposition rate with crystal monitors the thicknesses were usually within 20% of the values stated above.

The substrates used in this work were 75 mm diameter <100> Si wafers 0.38 mm in thickness. The wafers had a buffer layer of thermally growth SiO_2. Chips from each wafer are heat treated under 2 psi high purity He for various times at 700°C. Microstructural and analytical information on the samples was obtained with SEM/EDS (Topcon ABT 150/Oxford ISIS) and TEM (Philips EM400). Post processing line thicknesses on some chips were measured with a profilometer. However, this only determined the initial Nb thickness, and not the post heat treatment Nb_3Sn layer thickness. The crystal monitor accuracy was confirmed by TEM observation on a sample and by profilometry on a couple of test wafers to be within about 10 %. Critical currents were measured by a four point probe technique at 4.2 K in fields up to 7.5 T. Since there was some variation in minimum

Table I.

1. Si <100>
2. 100 nm of thermally growth SiO_2
3. 50-100 nm of Nb by e-beam evaporation
4. 350-400 nm of Nb or alloy by e-beam co-evaporation: Nb, Nb-La, Nb-Y, Nb-Ti, Nb-Ti-La, Nb-Sc-Al_2O_3, Nb-Dy, Nb-Dy-Ti
5. 400 nm of Cu by e-beam evaporation
6. 200 nm of Sn by evaporation or sputtering.
7. Wafer is cut into 15 x 15 mm^2 chips.
8. Heat treat 700°C for 30 minutes to 18 hrs.
9. 300 nm of Cu is applied for stability.
10. Each chip is patterned using photolithography and etching

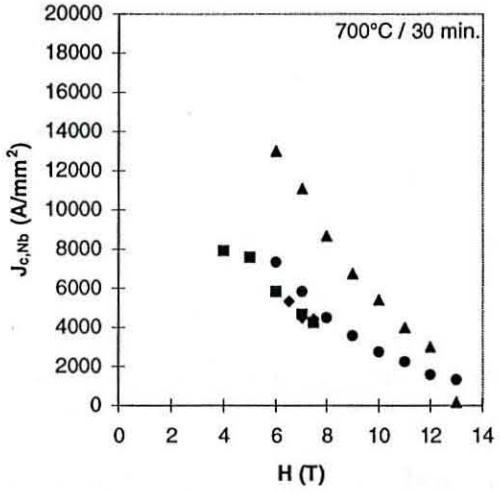
line width from chip to chip due to variation in etching and photoresist adhesion, the width of each line was determined by SEM observation after critical current testing. The $J_{c,Nb}$ reported here is the critical current divided by the initial Nb layer thickness and the measured line width.

RESULTS: CRITICAL CURRENT

The normalized critical current densities of films are shown in fig. 4. The film of fig. 4a is undoped while the films of figs. 4b, 4c, 4d, and 4e are Y-doped, Ti-doped, Sc-doped, and Sc-Al_2O_3-doped respectively. Since the Nb_3Sn layer thickness is not known the critical currents densities $J_{c,Nb}$ have been normalized to the initial Nb layer thickness (i.e. the as deposited Nb thickness). One can see that for the same heat treatment, 700°C for 30 minutes, the Ti-doped film has the highest $J_{c,Nb}$ while the undoped film has the least. Both doped films have higher $J_{c,Nb}$'s; however, without more information about the Nb_3Sn layer thickness it is difficult to conclude that the dopants have altered the microstructure. When the undoped material is heat treated for one hour its critical current density increases to values similar to the Y-doped sample. This suggests that the Nb layers are not completely reacted. Longer heat treatment times must be examined. However, this could produce strong interactions between the substrate and the films since most of the dopants will reduce the SiO_2 buffer layer resulting in the formation of Nb silicides. Nevertheless, the $J_{c,Nb}$ of the Ti-doped film is about a factor of three larger than the undoped film at all fields. If the growth rate of the Nb_3Sn in the Ti-doped films is three times faster than the undoped films, then most of the increase in $J_{c,Nb}$ could be accounted for by a difference in layer thickness. Since Nb will not carry any super current at these fields the J_c of the Nb_3Sn layer must be very large.

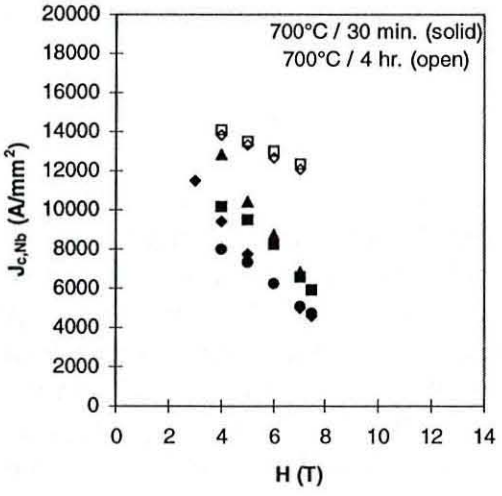
The flattening at low fields of the Ti-doped samples suggest that the samples were not stable and that they need more Cu. From the little high field data that was obtained it seems that the H_{c2} of the Ti doped material is not much higher that the undoped sample. This would suggest that Ti may not have substituted for Nb forming $(Nb,Ti)_3Sn$. Since Ti-doping effects are usually observed in fields above 12 T this will be explored further. The curves for the Y-doped and undoped films have about the same slope suggesting that Y does not affect H_{c2}. The films may also be in a tensile strain state due to a difference in the

coefficient of thermal expansion of the Nb, Nb_3Sn, and Si. This would depress J_c especially at higher fields. Work is underway to deposit films on single crystal MgO which has a better thermal coefficient of expansion match to Nb_3Sn.

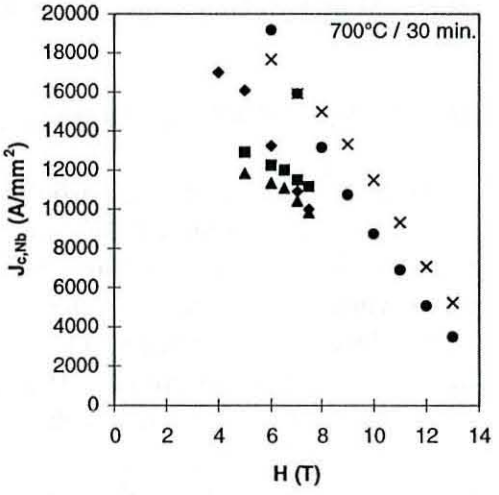


(a)

Fig. 4a. The critical current density of undoped films heat treated at 700°C for 30 minutes. The data has been normalized to its initial Nb layer thickness.

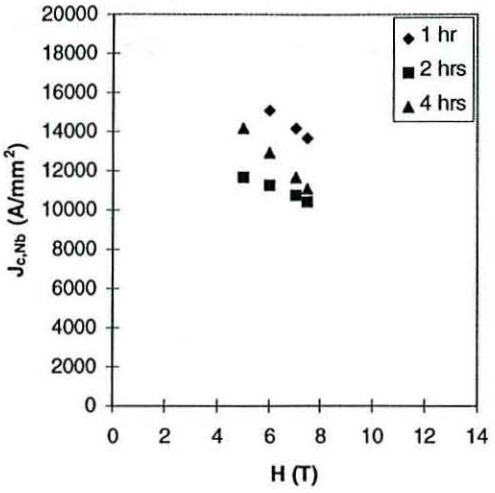


(b)

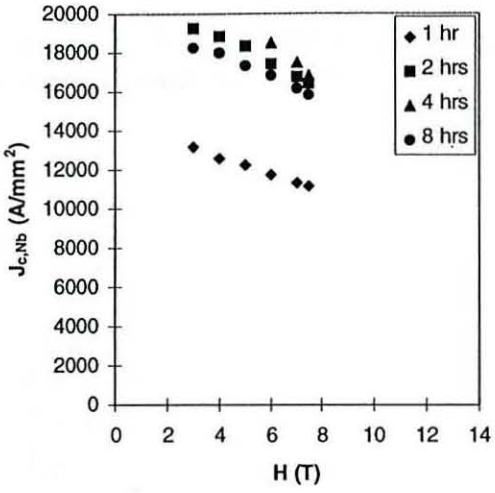


(c)

Figs. 4b and 4c. The critical current density vs. field of films heat treated at 700°C for 30 minutes. The data has been normalized to its initial Nb layer thickness. b) Y-doped and c) Ti-doped.



(d)



(e)

Figs. 4d and 4e The critical current density vs. field of films heat treated for various times. The data has been normalized to its initial Nb layer thickness. d) Sc-doped and e) Sc-Al_2O_3-doped.

The Sc-doped samples had very high critical current densities. A chip of the Sc-doped wafer heat treated for one hour had a $J_{c,Nb}$ of 1.4 x 10^6 A/cm^2 at 7.5 T (fig. 4d). The downward curvature of the data as it goes to lower fields suggest sample heating. As the heat treatment time is increased the critical current density decreases. The Sc-Al_2O_3-doped sample showed a different behavior. At 7.5 T several samples had $J_{c,Nb}$ greater than 1.5 x 10^6 A/cm^2. (fig. 4e). Some of the samples were heat treated for as long as eight hours. Microstructural analysis of the Nb_3Sn film showed that the grain size was very small, about 20 nm. More will be said about this wafer in the section on microstructure that follows.

RESULTS: MICROSTRUCTURE

To better understand the variation in J_c with heat treatment and additions (dopants) the microstructure of some of the films were observed by TEM (figs. 5 and 6). The Nb_3Sn grain size for most of the films was between 50-100 nm. The films with Ti had smaller grains while the Y-doped and the undoped had larger grains. The Sc-doped and Sc-Al_2O_3-doped films had the smallest grain size, about 20-25 nm, and these films produced some of the highest critical current densities, > 1 x 10^6 A/mm^2. The Sc-Al_2O_3-doped film also has small inclusions about 5 nm is diameter. From their shape and contrast they appear to be low density inclusions, which suggests an oxide of Sc or both Sc and Al. The results of this work are similar to the results obtained for doping done with Nb tapes. In that system the ZrO_2 inclusions inhibited grain growth during heat treatments at 1000-1100 °C.[2, 3]

Prior work on e-beam co-evaporation of Nb-Sn-Al_2O_3 films by Hammond et al. also had inclusions.[4] However, in that work the three materials Nb-Sn-Al_2O_3 were co-evaporated onto a heated substrate to produce Nb_3Sn. This fabrication method produced a Nb_3Sn film with larger grains, about 54 nm. The makeup of this sample is still not well understood since the composition was not controlled during sample fabrication as the Al_2O_3

came from the crucible of the e-beam evaporation system. Nevertheless, the high J_c correlates with a very small grain size. This data shows that a high critical current density can still be achieved and a peak in the maximum pinning force for Nb_3Sn grains smaller than 20-25 nm has yet to be reached. The work by Hammond et al. suggested that the J_c would drop for grain sizes less than 40 nm.

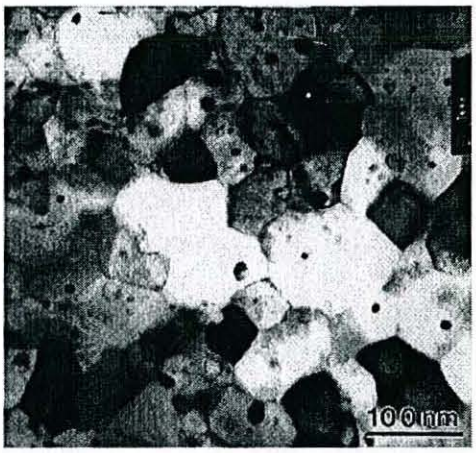
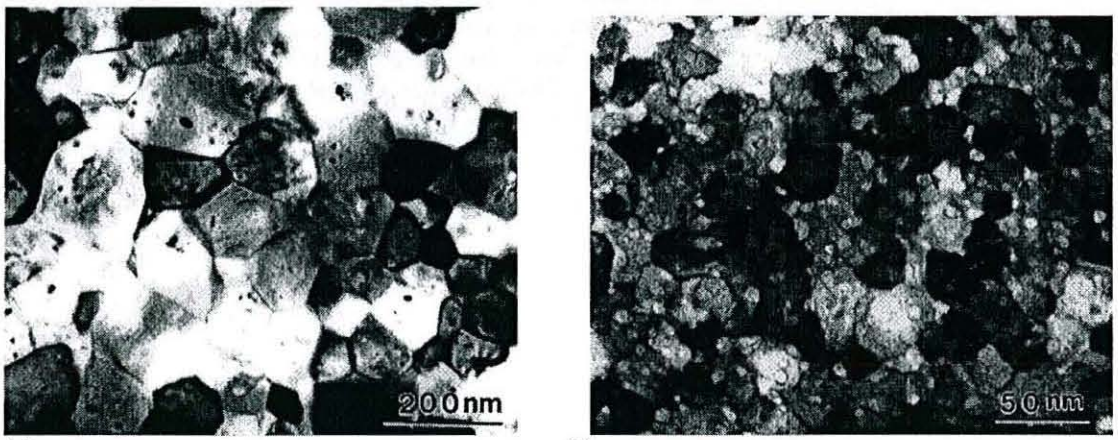


Fig. 5. TEM image of undoped sample heat treated for 700°C for 30 min.



(a) (b)

Fig. 6. TEM images of (a) Ti-doped Nb_3Sn and (b) Sc-Al_2O_3-doped.

CONCLUSIONS

This work has developed a thin film process to simulate a bronze-type fabrication method used to produce wires in uniform films. Engineered microstructures have been produced in Nb_3Sn which carry very high critical current densities, greater than 1 x 10^6 A/cm^2 at 4.2 K and 7.5 to 10 T. The grain size of the Nb_3Sn in some of the films shows that J_c can still be high for a grain size of 20 nm.

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REFERENCES

1. D.R. Dietderich and R.M. Scanlan, "Characterization of Superconductors with Artificial Pinning Microstructures," *IEEE Transactions on Applied Superconductivity*, Vol. 5, no. 2, pp. 1777-1780, June 1995.
2. E.L. Hall, M.G.Benz, L.E. Rumaner, and K.D. Jones, "Interface Structure, Grain Morphology, and Kinetics of Growth of the Superconducting Intermetallic Compound Nb_3Sn," GE Research & Development Center, Materials Characterization Laboratory, Report Number 90CRD265, December 1990.
3. L.E. Rumaner, E. L. Hall, M.G.Benz, "The Role of Oxygen and Zirconium in the Formation and Growth of Nb_3Sn Grains," *Metallurgical Transactions*, Vol. 25A, pp. 213-219, January 1994.
4. R.H. Hammond, B.E. Jacobson, T.H. Geballe, J. Talvacchio, J.R. Salem, H.C. Pohl, and A.T. Braginski, "Studies of Electron Beam Co-evaporation of Nb_3Sn Composites: Critical Current and Microstructure," *IEEE Transactions on Magnetics*, Vol. MAG-15, no. 1, pp. 619-622, January 1979.