Use of electron beam lithography to selectively decompose metalorganics into patterned thin-film superconductors

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Fine line superconductors, approximately 5 μm in width and 260 nm thick, were formed from Y-Ba-Cu on $\langle 100 \rangle SrTiO_3$ by the combined methods of metalorganic deposition and selective area electron beam exposure. The lines were written in metal neodecanoates using an electron beam having a spot size of 0.25 μm and an energy of 25 kV. The dosage of the exposure was 1200 $\mu C/cm^2$. Unexposed areas were removed with a 30 s xylene wash. A 500 °C pyrolysis in air for 300 s followed by rapid thermal annealing in oxygen produced lines having superconducting onsets above 90 K and zero resistance at 69 K.

The first applications of the new high T_c materials[1-5] will undoubtedly be in the form of thin-film devices such as superconducting quantum interference devices (SQUID's),[6] integrated circuit interconnects,[7] and infrared detectors.[8] Before full benefit of the new materials can be exploited and thin-film devices can be fabricated, it is essential that methods of patterning thin films of these materials be developed. Current patterning techniques have included scribing, wet chemical etching,[9] reactive ion etching,[10] local laser ablation,[11] ion beam amorphization,[6] and, most recently, selective laser[12] and ion beam[13] decomposition of organics which form thin-film superconductors.

Many thin-film organic materials are highly sensitive to electron beam bombardment,[14] which renders them insoluble in their starting organic solvents. Unlike ion beam patterning,[13] which can cause sputtering of the organics prior to pyrolysis or laser patterning,[12] which requires that the organic films have high-energy absorbance to prevent substrate damage during the writing process, high-energy electron beams have large penetration depths with no apparent adverse effects to the substrate.

In this letter we describe how electrons beams were used to selectively decompose metalorganics (MO) into patterned Y-Ba-Cu thin-film superconductors. Selective MO patterning was accomplished by electron beam exposure of 4.4-μm-thick metal neodecanoate films with 25 kV electrons at a dose of 1200 $\mu C/cm^2$. The exposure rendered the organic film locally insoluble in xylene, the MO solvent, thus permitting selective area patterning prior to pyrolysis. The patterned MO was developed in xylene for 30 s, pyrolized at 500 °C for 300 s in air, then rapid thermal annealed in oxygen. Fine lines, approximately 5 μm in width and 260 nm thick, were patterned on $\langle 100 \rangle$ $SrTiO_3$ and were found to have superconducting onsets above 90 K and zero resistance at 69 K.

Neodecanoates of Y and Ba were formed by reaction of their metal acetates with ammonium neodecanoate. Copper neodecanoate was formed by reaction of copper(II) acetate with tetramethylammonium neodecanoate. The individual metal carboxylates were dissolved in a mixture of xylene and pyridine, then combined together to form a single solution which formed thin films having the metal ratios Y:Ba:Cu of 1:2:4.[15] Details describing the preparation of the neodecanoates and the formation of thin-film superconductors from these materials may be found elsewhere.[13,16,17]

The solution of the combined neodecanoates, when used to form films 1.5 μm thick after pyrolysis and rapid thermal annealing, had superconducting onset temperatures above 90 K and zero resistance at 86 K.[17] In the present experiments the combined neodecanoates, dissolved in xylene and pyridine, were spun onto single crystals of $\langle 100 \rangle SrTiO_3$ at 2000 rpm for 30 s. The soft organic film was baked at 150 °C for 15 min to drive off the xylene and pyridine, leaving a film 4.4 μm thick which was soluble in xylene. A JEOL JBX-

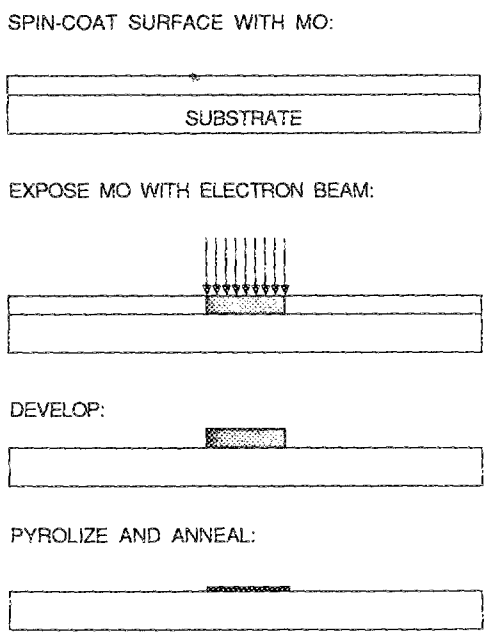

FIG. 1. Schematic of the electron beam patterning sequence consisting of selective electron exposure, development, and pyrolysis/annealing.

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5D11(F) electron beam microfabricator was used for selective area electron beam exposure. The beam energy was 25 kV, the spot size 0.25 μm, and the current 1000 pA. Xylene was used as the developer. Pyrolysis of the MO was done in air at 500 °C for 300 s,[13,16,17] forming thin films of the combined oxides 260 nm thick. The samples were rapid thermal annealed in oxygen at 850 °C for 60 s followed by a second anneal in oxygen at 920 °C for 30 s.[17] The patterning sequence is shown schematically in Fig. 1.

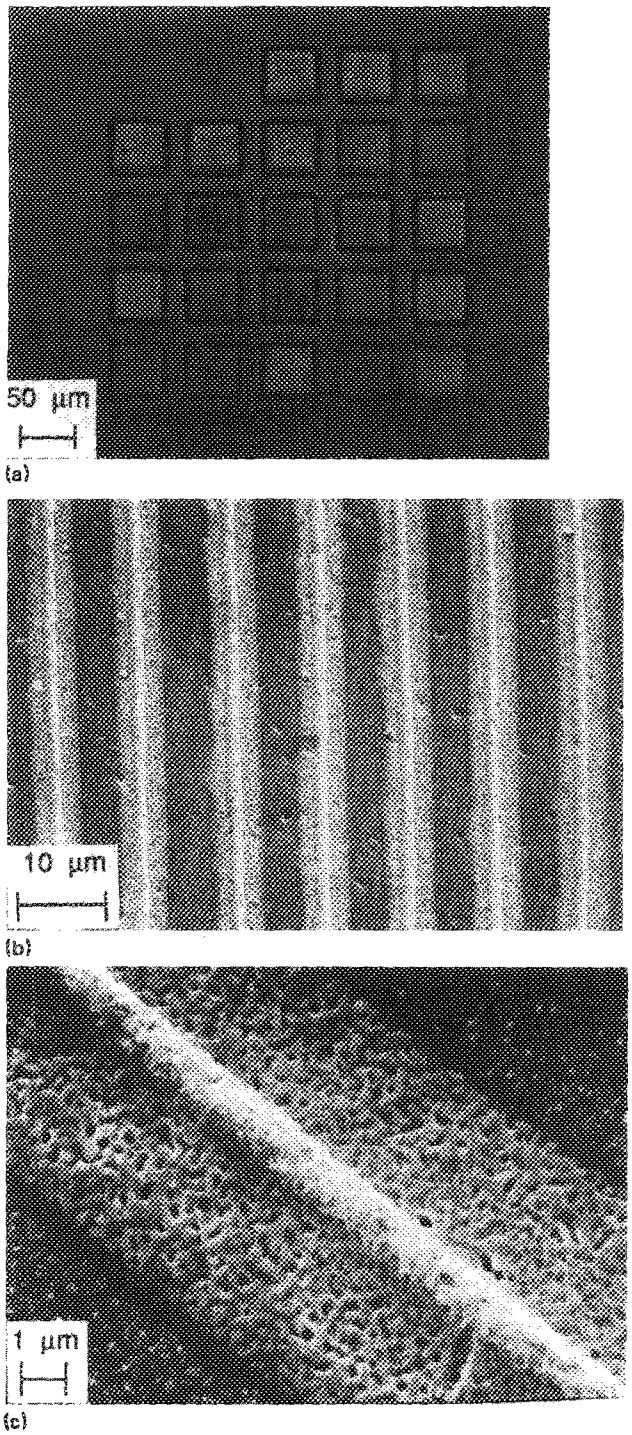

FIG. 2. (a) Selective 50 μm × 50 μm square area electron beam exposures using 25 kV electrons, a 0.25 μm spot size, and a beam current of 1000 pA. Dosage increases from 410 to 2000 μC/cm^2 in increments of approximately 66 μC/cm^2. Increasing dosage is from left to right, top to bottom, with the upper left corner being the lowest dose. The film was developed in xylene, but has not been pyrolized. (b) Patterned 5 μm lines. The metalorganic was developed in xylene for 30 s, pyrolized in air at 500 °C for 300 s, then rapid thermal annealed in oxygen. (c) Magnified view of one of the lines showing the central region of exposure and the effects due to beam broadening.

Figure 2(a) shows the results, after development but prior to pyrolysis, of a series of exposed 50 μm × 50 μm squares. Dosages range from 410 to 2000 μC/cm^2 in increments of approximately 66 μC/cm^2. The dosage increases from left to right and top to bottom with the lowest dose being at the upper left. As can clearly be seen from Fig. 2(a), dosages of 410 and 476 μC/cm^2 were insufficient to render the MO insoluble in xylene.

Dosages less than 1000 μC/cm^2 produced films which would delaminate from the $SrTiO_3$ surface upon pyrolysis. Dosages equal to or in excess of 1200 μC/cm^2 produced films which strongly adhered to the $SrTiO_3$ surface following pyrolysis. All subsequent patterning work was done with a dosage of 1200 μC/cm^2 to minimize exposure time.

Figure 2(b) shows a typical set of 5 μm lines after electron beam exposure, development, pyrolysis, and rapid thermal annealing. The lines were written as 1 μm lines with a beam energy of 25 kV and a spot size of 0.25 μm. Figure 2(c) is a magnified view of one of the lines, showing the central region of exposure together with extensions of the superconducting material on either side of the line. The smearing of the line is due to the use of thick metal oxide precursor films (4.4 μm). Significant beam broadening due to electron scattering occurs as the focused beam traverses the metal neodecanoate layer.

In Fig. 3 we have plotted resistance as a function of temperature for 100 lines electrically connected in parallel but with each line spatially separated from its neighbor by a center-to-center distance of 10 μm. All lines were approximately 5 μm in width. A superconducting onset was seen above 90 K. The 5 μm lines became fully superconducting at 69 K. The broadened transition to full superconductivity is believed to arise from interaction of the thin film with the $SrTiO_3$ substrate.[13,16,17] Strontium substitution for Ba has been shown to reduce the superconducting transition temperature in Y-Ba-Cu superconductors.[18,19]

Attempts to produce finer superconducting lines by using thinner unpyrolized neodecanoate films or by developing

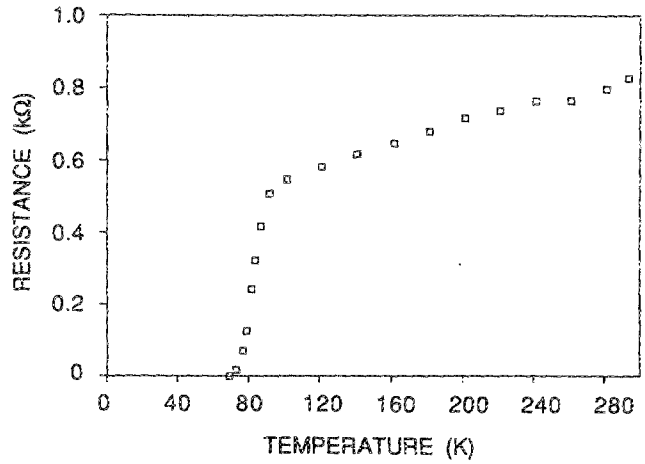

FIG. 3. Resistance as a function of temperature for 100 lines electrically connected in parallel, but with each line spatially isolated from its neighbor by a center-to-center distance of 10 μm. The lines are approximately 5 μm in width.

longer in xylene after electron beam exposure have proved unsuccessful to date. In the former case the lines formed were found to have even broader superconducting transitions, while in the later experiments the lines were removed during developing. We are presently exploring other processing techniques for patterning.

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