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A technique or pattern YBCuO utilizing rapid thermal annealing to intermix layers such as silicon with the superconductor was analyzed. Films wer prepared using laser ablation, and e-beam deposition. Areas that intermixed destroyed the superconductivity and allowed 10 micron lines to be fabricated. The system was evaluated using SEM, Auger; XPS and X-ray diffraction. Another technique was investigated in which silicon films were deposited and pattern over existing YBCuO films. The silicon was patterned and then annealed to define micron-sized superconducting patterns. This technique is relevant to producing large-area superconducting patterns such as delay lines, microwave devices, and packaging interconnects.

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Technical Abstract:

A technique to pattern YBCuO utiiizing rapid thermal annealing to intermix layers such as silicon with the superconductor was analyzed. Films were prepared using laser ablation, and e-beam deposition. Areas that intermixed destroyed the superconductivity and allowed 10 micron lines to be fabricated. The system was evaluated using SEM, Auger, XPS and x-ray diffraction. Another technique was investigated in which silicon films were deposited and patterned over existing YBCuO films. The silicon was patterned and then annealed to define micron-sized superconducting patterns. This technique is relevant to producing large-area superconducting patterns such as delay lines, microwave devices, and packaging interconnects.

I. INTRODUCTION

This report covers the Phase I progress on "Novel Si-YBCO Reactive Patterning Technology for Manufacturing of Large Area High Tc Superconducting Electronic Devices." In this report we will review the patterning technology, look at SEM, Auger and XPS analysis of patterned materials, report on the simplified "reverse patterning technique", introduce MGO buffer layers, and discuss applications of this work.

We will also report on some preliminary data by Prof. Chan on Cerium Oxide deposition on Si (111) and on R sapphire. Dr. Ma of Columbia University and the University of British Columbia also consulted on this work and holds the original patents utilizing rapid thermal annealing to quench the superconductivity.(1)

II. MATERIAL PROPERTIES OF SI-YBCO INTERMIXED SYSTEMS

A. Review of Patterning Procedure

Figure 1 and Figure 2 review the rapid thermal annealing patterning process. In Figure 1 a Au or Ag buffer layer is patterned onto Silicon wafers directly, either by liftoff or chemical etching. YBCO is deposited by either e-beam sequential deposition, sputtering or laser-ablation, followed by rapid thermal annealing. Depending on the time and temperature sequence of the anneal, the silicon interacts with the YBCO causing it to become insulating whereas the area over the "buffer" stays superconducting. Figure 2 demonstrates a similar procedure except an insulating substrate is utilized such as MgO, and the silicon is

deposited and patterned before the High Tc film is applied and annealed.

B. Materials Characterization

Two systems were investigated; one is a YBCO film on a silicon buffer layer which were deposited on MgO, and the other is YBCO deposited on Si directly. This system is chosen so we can analyze the behavior between films directly on a buffer layer and intermixed with silicon. This system and similar ones are of interest for microwave devices on dielectric substrates. The Si-YBCO system is of interest for superconductor-semiconductor devices and packaging interconnections.

On the MgO substrate the Si-YBCO intermixed films appeared light gray and were slightly transparent after annealing. The pure YBCO films were black and opaque. The resistivities of the films at room temperature were at least five to six orders of magnitude higher than pure YBCO films. The electrical properties depended significantly on the silicon buffer thickness. For a 200A silicon layer, the mixed film was conductive, but not superconducting. For a 4000A thick YBCO film the minimum thickness required for the Si layer to make a good insulating film was 500A. This corresponds to a composition ratio of 1:1 for Si:YBCu.

The microstructure of the intermixed system was examined by SEM and X-ray Diffraction measurements. Figure 3A shows a pure YBCuO film on MgO. Note the polycrystalline structure with a grain size of a few microns. With a 500A silicon layer after intermixing most crystalline domains are absent as can be seen in Figure 3B.

When the Si layer is raised to 800A (corresponding to a composition ratio of 1.2:1 for Si:YBCuO) the film contained many small white spots of a half micron in size as shown in Figure 3C. The crystalline structure is completely disrupted and this was confirmed by X-ray diffraction measurements. Figure 4a shows the x-ray diffraction pattern for pure YBaCuO and Figure 4b shows the pattern with 500A silicon mixing. The peak intensities of the YBCuO 123 phases are significantly reduced for the Si mixed film, and much of the 123 phase converted to 211 phase. In general the 123 phase is chemically unstable compared with 211 and CuO phase in the presence of silicon.

C. XPS and Auger Analysis

The reactions that occur during annealing are driven by the thermodynamics of the material system. Table I lists the heat of formation of the metallic oxides.

Table I Heat of Formation of Metallic Oxides in kcal/mole(2)

Metal Oxides	SiO_2	BaO	CuO	Y_2O_3
Heat of Formation	-209.9	-134.6	-37.7	-419.6

From the heat of formations one can see that Si will react with oxygen bound to either Ba or Cu. Therefore during the annealing process silicon will reduce the YBaCuO and form Silicon oxides. When the sample undergoes a high-temperature rapid thermal anneal the elements interdiffused in the $Cu/BaO/Y_2O_3/Si$ layers and formed

a homogeneous film. The silicon diffused throughout the entire film and reacted with oxygen during the annealing. This was confirmed by XPS data and is shown in Figure 5. Figure 5 shows the Si 2p XPS for a 500A Silicon mixing after annealing. The peak position of the Si 2p core level is shifted to high binding energy of 103.0 ev, very close to SiO_2 at 103.4 ev, rather than to pure silicon at 99.2 ev. The energy difference is about 3.8 ev which agrees with data of Hill(3). This indicates the silicon is fully oxidized. Ion sputtering with 3 keV Ar ion beam with a sputtering rate of approximately 15A/min shows the peak position to be stable for about 1/2 the thickness of the film. This indicates that the silicon oxide formed during annealing is throughout the film and causes it to become insulating.

D. Silicon Substrates-Microstructure

The formation of superconductor-semiconductor devices and packaging interconnects on silicon would be feasible if high Tc superconducting materials could be directly patterned. The interdiffusion is usually sufficient to destroy superconductivity and necessitates the use of a buffer layer, as shown in figure 1. A series of different annealing cycles directly on Si(100) are shown in Figure 6. At 930 degrees for 30 seconds intermixing starts to occur, and at 950 degrees the layers intermixed completely. The polycrystalline grains of the film are separated by many white spots which may be silicon oxides. The lattice constant of Si is 5.43A, and for YBaCuO the lattice constant is a/b=3.82/3.84A, c=11.72A. The thermal expansion coefficients are

2.5×10^{-6} for Silicon and 1.7×10^{-5} for YBaCuO.(4,5) This large difference in constants causes the layer to be strained and microcracks appear. This allows silicon to outdiffuse forming oxides on the surface and between the grains, producing a non-superconducting film. Figure 6d shows a film with a Au buffer layer which did not indicate any formation of silicon oxides.

Auger depth profiles of four samples annealed under different conditions are shown in figure 7. With the 900 degree anneal there is slight diffusion of the Ba and Cu but not the Yttrium. The resistivities of these samples were semiconductor-like. As the annealing temperature was raised the silicon intermixed. A superconducting transition temperature of 85K was seen in sample(b) but it was not complete. At 980 degrees the film became insulating. With a Au buffer layer of 2000A, the silicon diffusion was suppressed, and the film became completely superconducting.

E. Cerium Oxide Buffer Layers

Preliminary work was done to identify easily deposited buffer layers that would be compatible with silicon processing. CeO was deposited on Si(111) and annealed in-situ at 720C. A TEM micrograph at 20,000x is shown in figure 8, including the ring structure obtained showing CeO_2 rings on Si(111). These non-metallic buffers will provide suitable buffers for device manufacture.

III. REVERSE PATTERNING TECHNIQUE

A simplified way of patterning films of YBaCuO previously deposited by either e-beam, sputtering or laser ablation on to a insulating substrate is to deposit a Si pattern utilizing lift-off techniques (by e-beam evaporation) followed by rapid thermal annealing. The process is demonstrated in figure 9. Samples were processed with rapid thermal annealing at 950-980C for 20-60 seconds. The area left uncovered remained superconducting. This process is much easier for fabrication than etch of the high Tc material. Linewidths are limited by the lateral diffusion of the Silicon.

Structures were fabricated on laser-ablated YBCuO, utilizing e-beam evaporated Si, and rapid thermal annealing. YBCuO was deposited on $SrTiO_3$ by laser ablation to a thickness of 1500A followed by e-beam evaporation of a 400A Si film. The film was annealed at 970C for 30 seconds in oxygen. Figure 10 shows 10 micron lines. The Si covered regions intermixed forming an insulator with a resistance greater than 20Megaohms.

Figure 11a shows the resistivity of a 10 micron by 200 micron line structure, and figure 11b shows the original laser ablated film. Both curves are almost identical and show the same Tc of 87K. The critical current density of the lines were over 10^6 A/cm^2 at 77K. This suggests that a short rapid thermal anneal does not disturb the film properties and that this is a successful way to pattern films.

IV. MGO BUFFER LAYERS ON SILICON

Initial work was done on utilizing MgO buffer material to replace either Au or Ag. The MgO has a good lattice match to YBaCuO and is stable at high temperature. An MgO film was sputtered onto Si(100) and patterned using chemical etching. YBCuO was deposited on the film and annealed by rapid thermal process. The same conditions were used as for Au buffers. The MgO layer was between 1000-2000A, and the YBaCuO was 4000A. The Tc was 82K and the Jc was 5 x 10^4 A/cm^2 at 77K. This film is shown in figure 12. These values are much better than the patterned films obtained with Au buffers, as reported in the Phase I proposal.

V. DISCUSSION OF THE TECHNIQUE

This technique can be very effective and can be utilized with films deposited by either sputtering, e-beam or laser ablation. Previous work has indicated that e-beam sequential layer films can be deposited over fairly large areas with good uniformity. We feel that these procedures, combined with e-beam evaporation could produce devices, such as delay lines, packaging interconnects, etc. that would require up to 3 square inches of active area.

A disadvantage of this process is the requirement for post-annealing which can have a detrimental effect on Tc and Jc. This technique does not require chemical etchants which can be detrimental to system integration. This procedure should be

preferred for hybrid structures and packaging interconnects.

With the proper buffer layer these procedures can be utilized to pattern microwave devices on sapphire and other substrates. The Cerium Oxide buffer layers have been deposited on R-sapphire successfully. This patterning procedure would conform to these systems.

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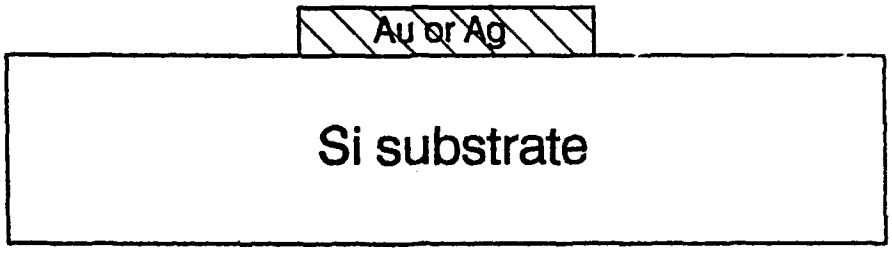
6. Ma, Q.Y. and Weinman, L.S., (to be submitted to Applied Physics Letters)

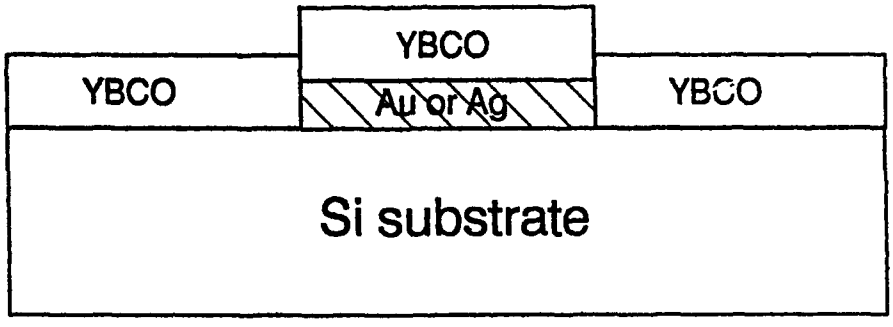
LIST OF FIGURES

Patterning of HTS film on Si

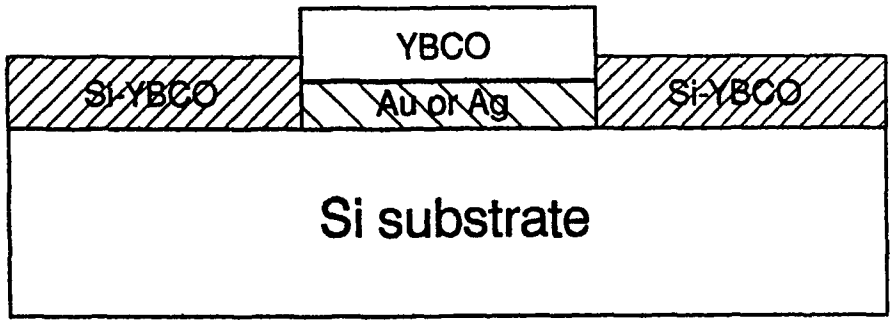
Patterning of buffer layer



Deposition of YBaCuO film



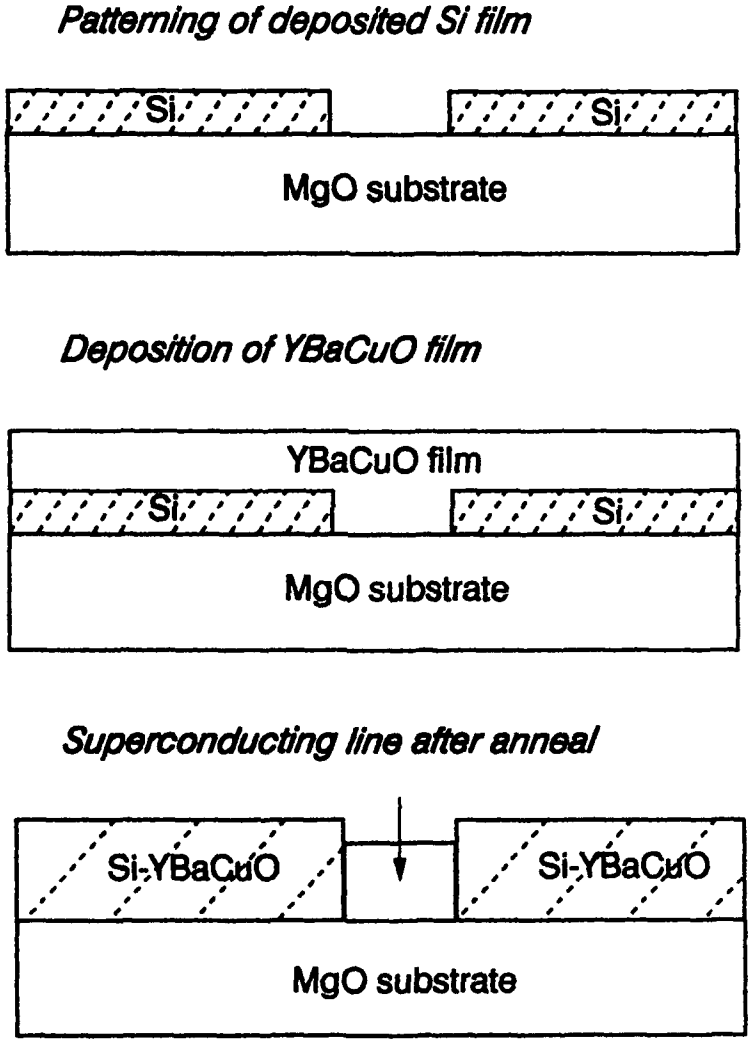
Superconducting line after anneal



Scheme of the patterning process for making HTS YBaCuO device structures on Si substrates.

Figure 1

Patterning of HTS film on MgO

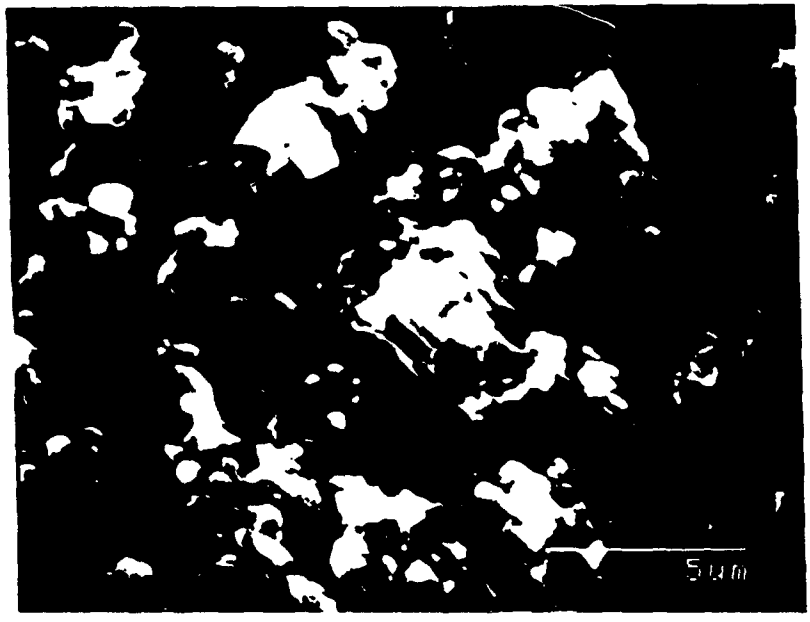


Scheme of the patterning process for making YBaCuO device structures on oxide insulating substrates.

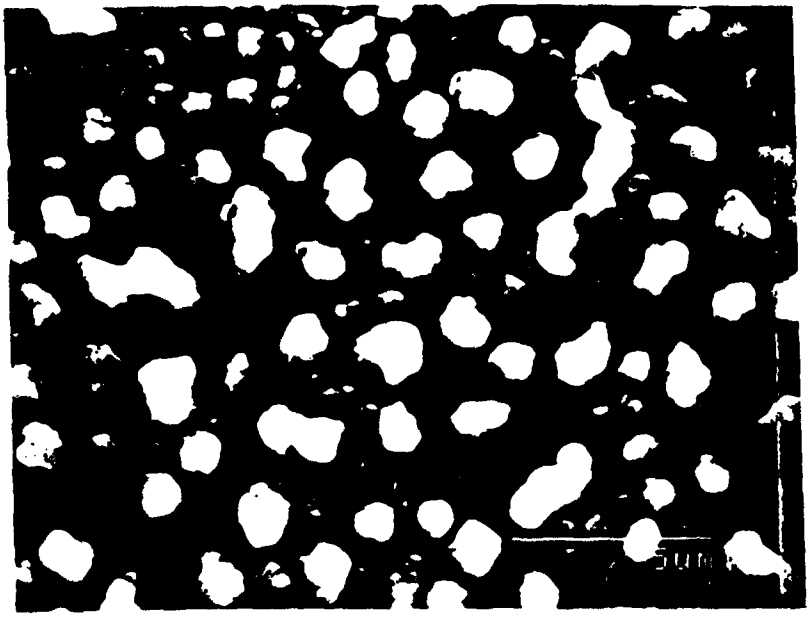
Figure 2

(a)

(b)

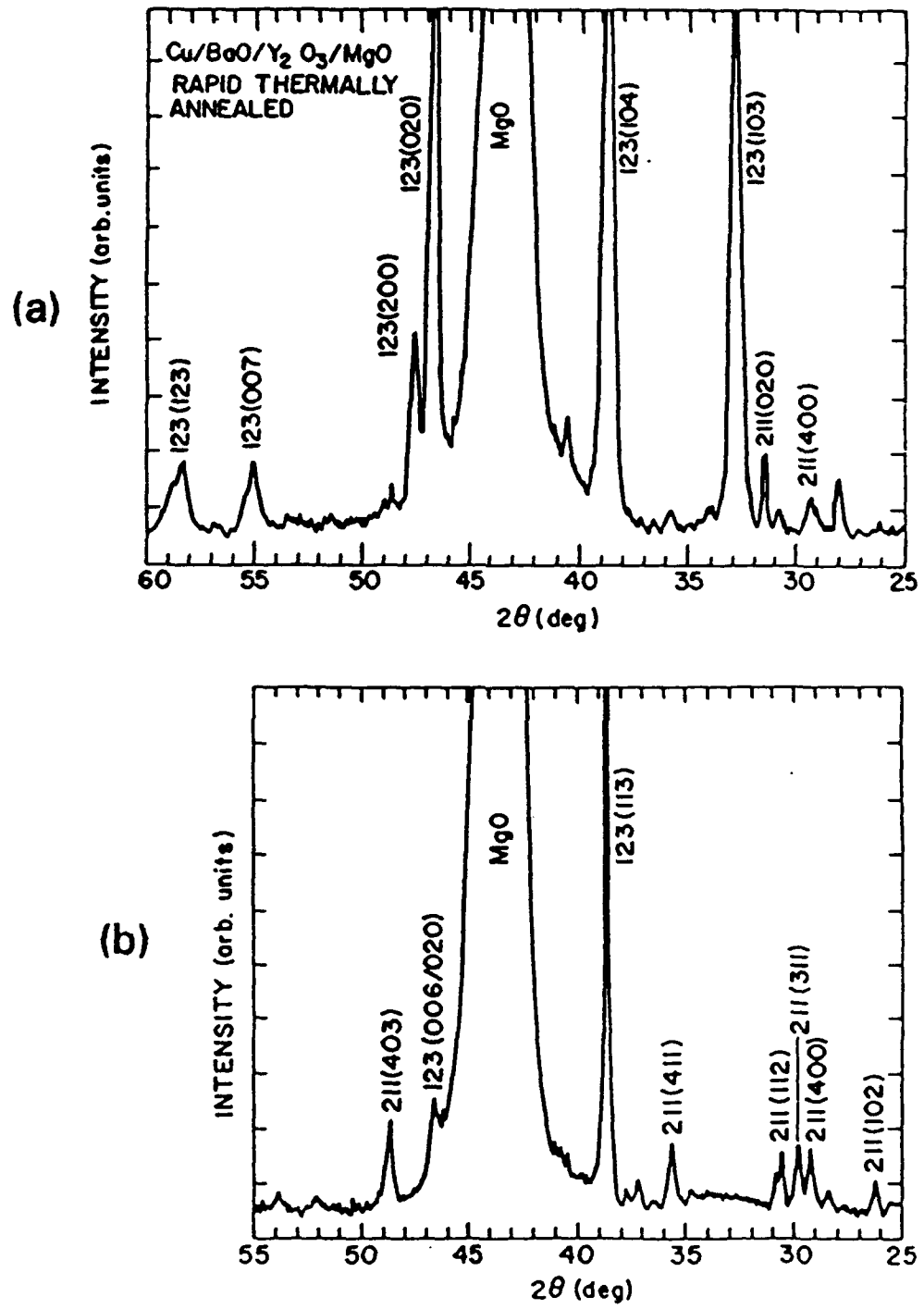


(c)



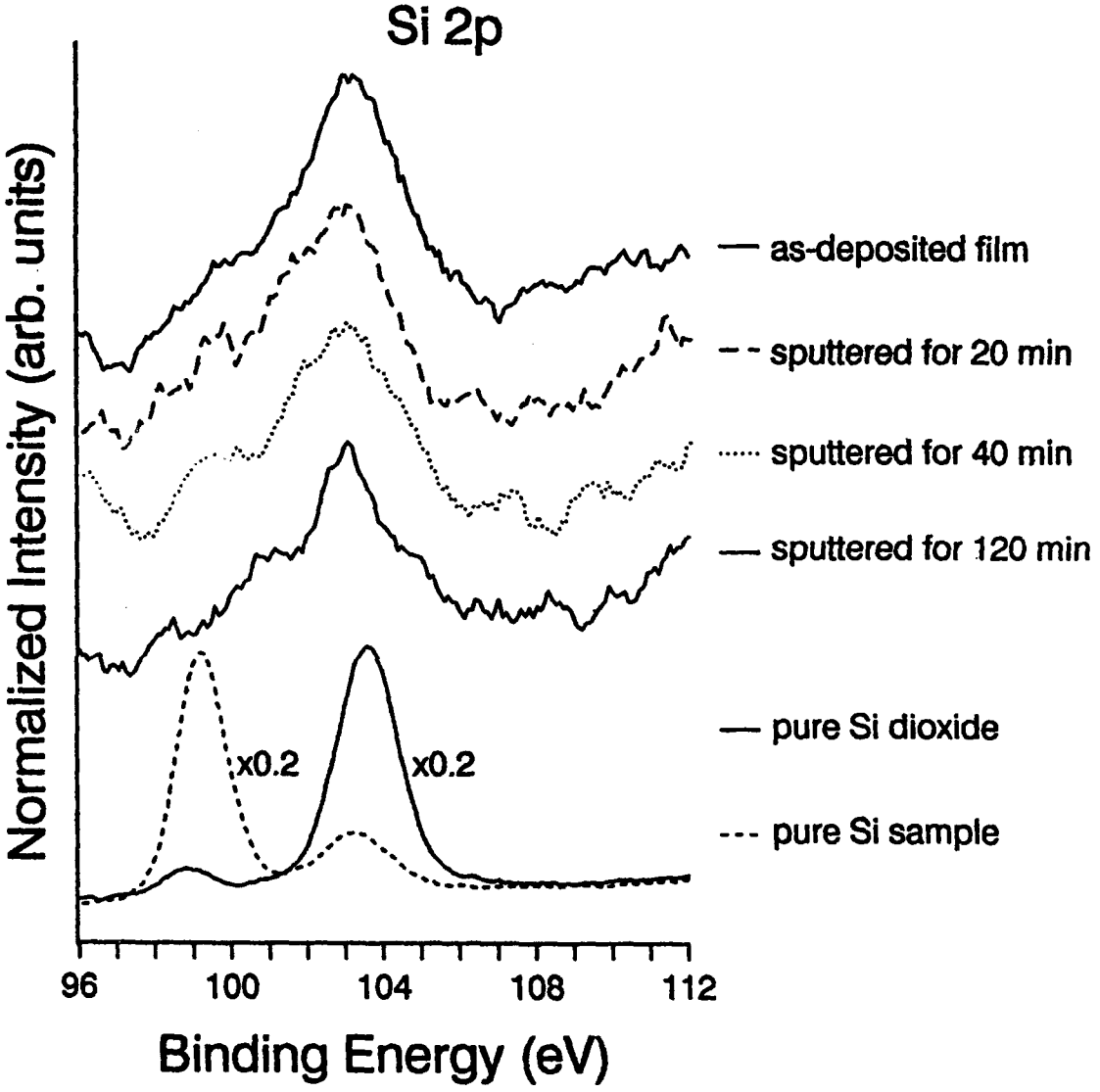
Scanning electron micrographs of (a) a pure YBCO film on MgO with 980°C 45s RTA, (b) the same film intermixed with 500 Å Si, and (c) with 800 Å Si, showing the reaction of Si with YBCO and formation of Si oxides.

Figure 3



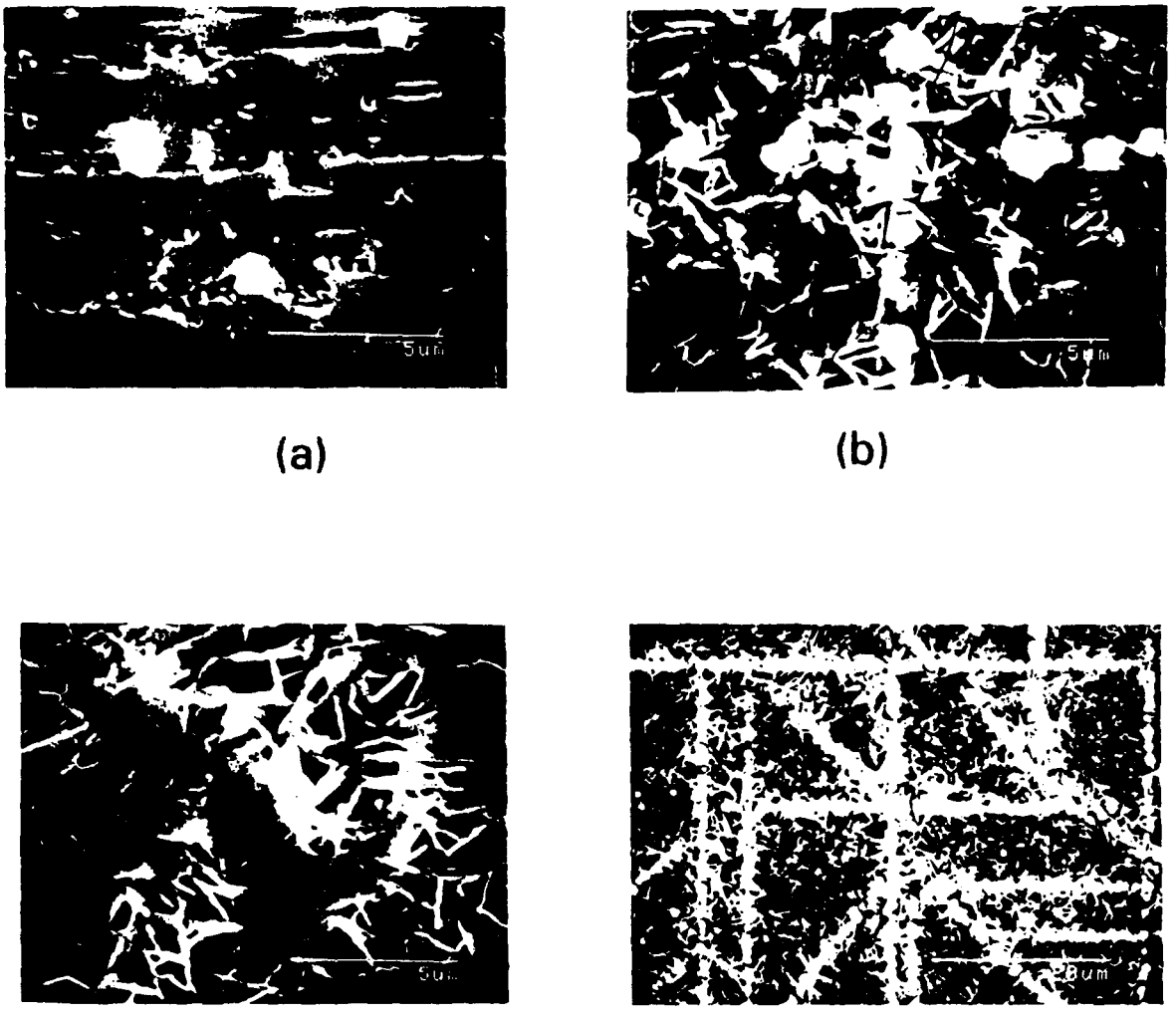
X-ray diffraction pattern of (a) a pure YBaCuO film on MgO showing mainly the 123 phases, and (b) a Si-YBaCuO intermixed film showing great reduction in the peak intensity of the 123 phase.

Figure 4



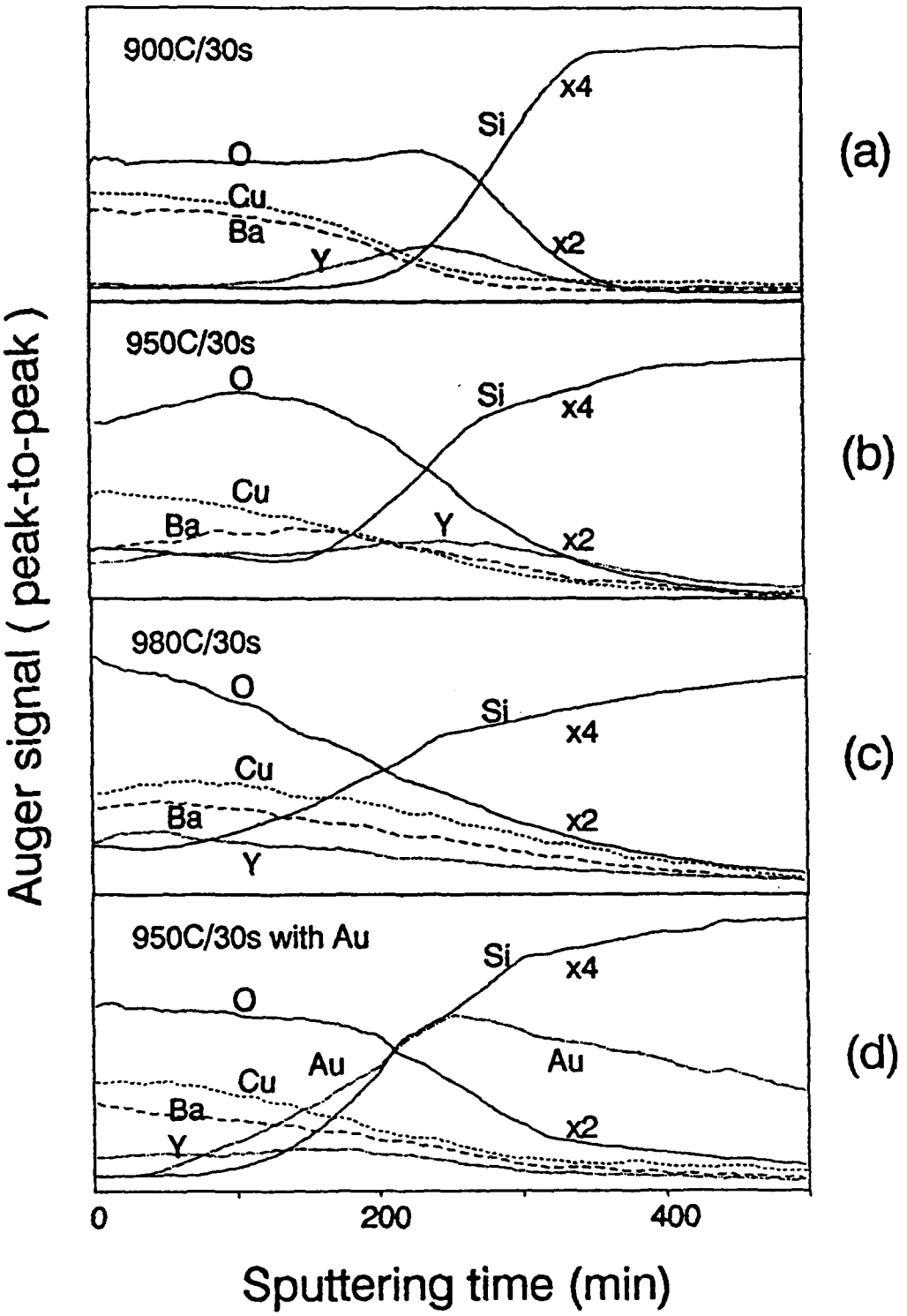
XPS spectra of Si 2p core level from (a) the surface a Si-YBaCuO intermixed film, and the film after (b) 20 min; (c) 40 min; and (d) 120 min sputtering. The peak position is close to pure SiO_2 peak (e), rather than pure Si peak (f). This indicates the formation of Si oxide in the Si-YBaCuO system.

Figure 5



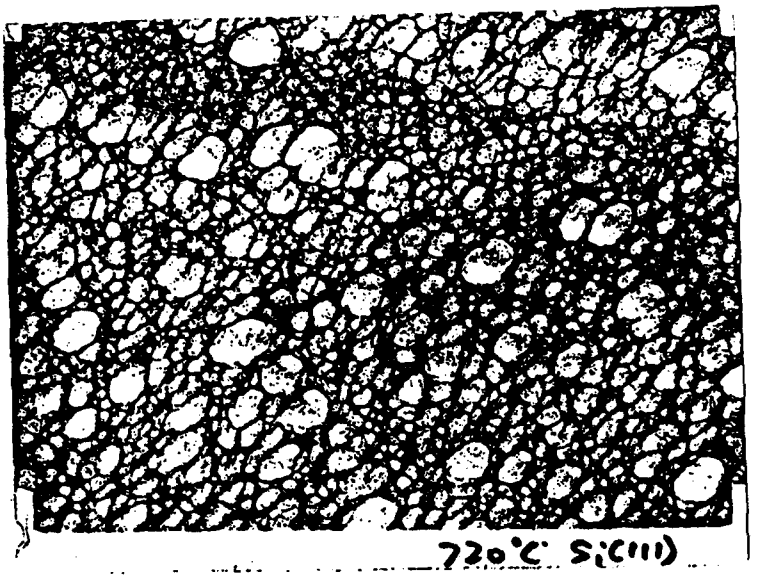
Scanning electron micrographs of a YBCO film deposite directly on a Si substrate. A film processed with (a) a 930°C, 30s RTA; (b) a 950°C, 30s RTA; (c) some as (b) but view from a large scale; and (d) a film processed at 950°C for 30 s and with a 1000 Å Au buffer layer.

Figure 6



Auger depth profiles of a YBCO film on a silicon substrate with; (a) 900°C, (b) 950°C, and (c) 980°C annealing for 30s, (d) 950°C with a 1000 Å Au buffer layer.

Figure 7



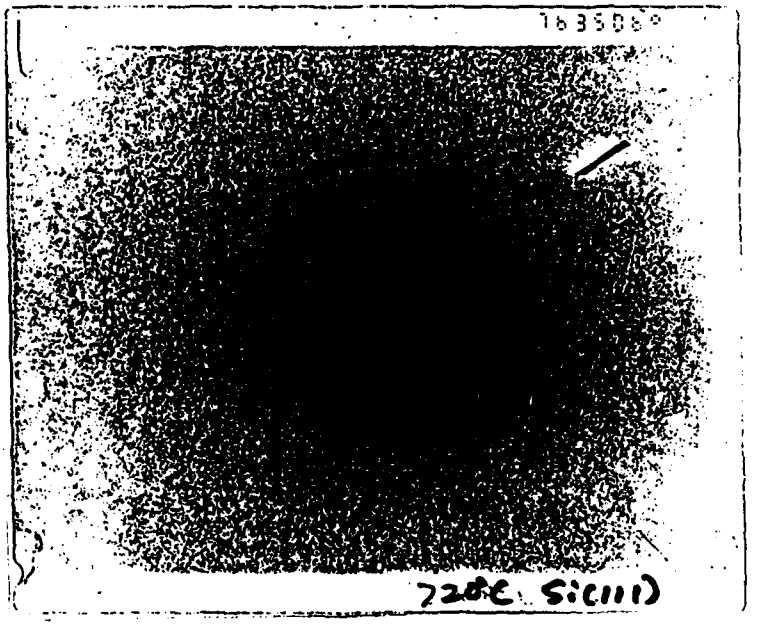
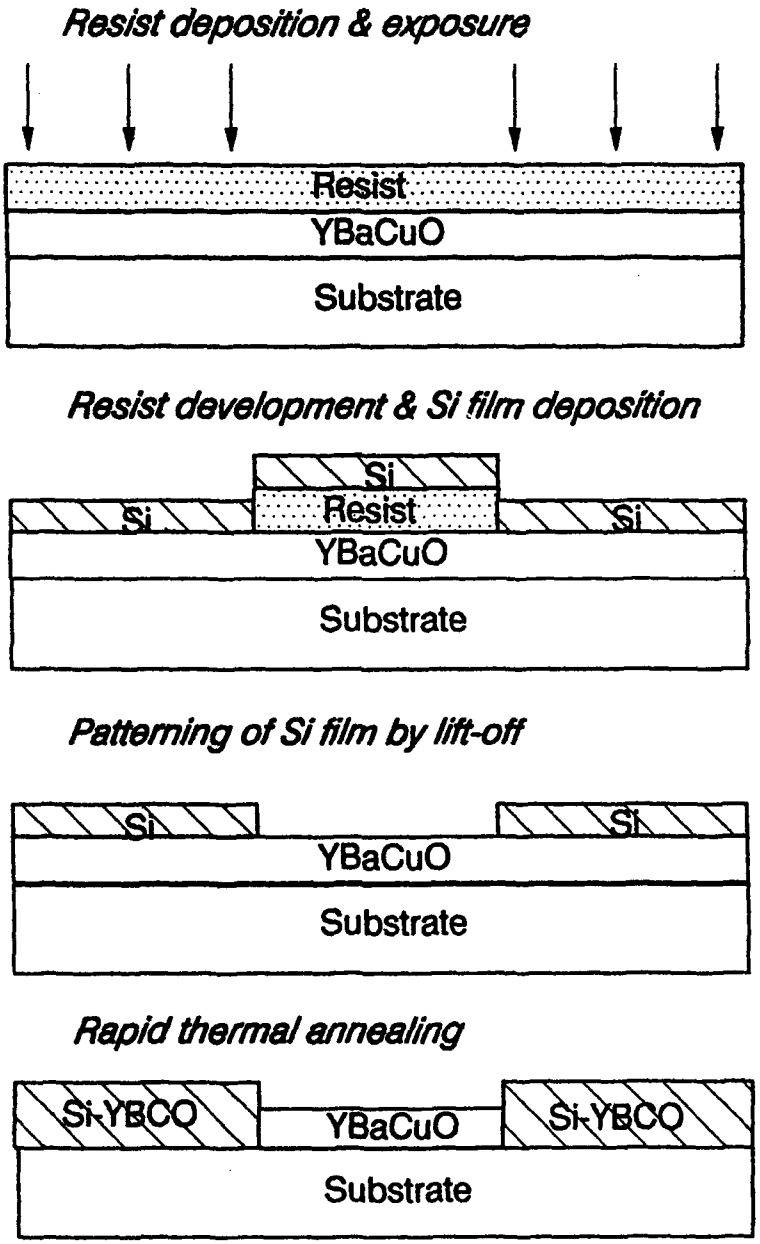


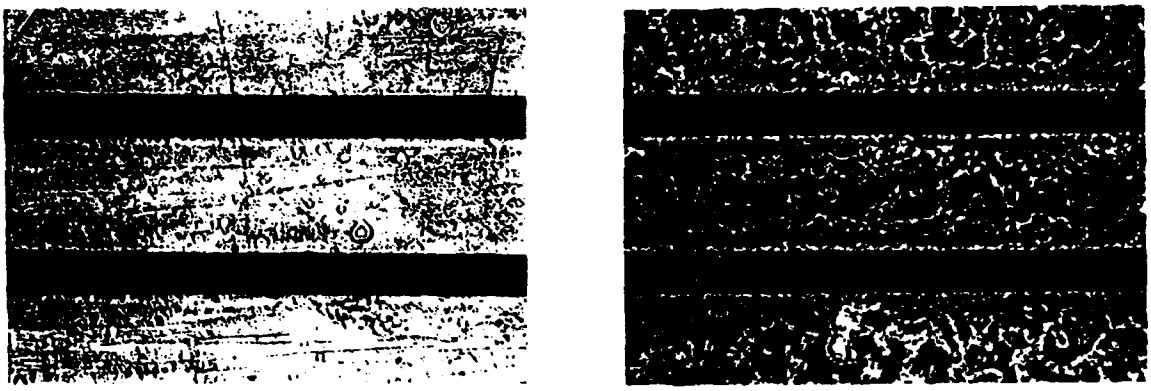
Figure 8

Reverse Si-YBCO Reactive Patterning



Scheme of the reverse Si-YBCO patterning process for making HTS device structures.

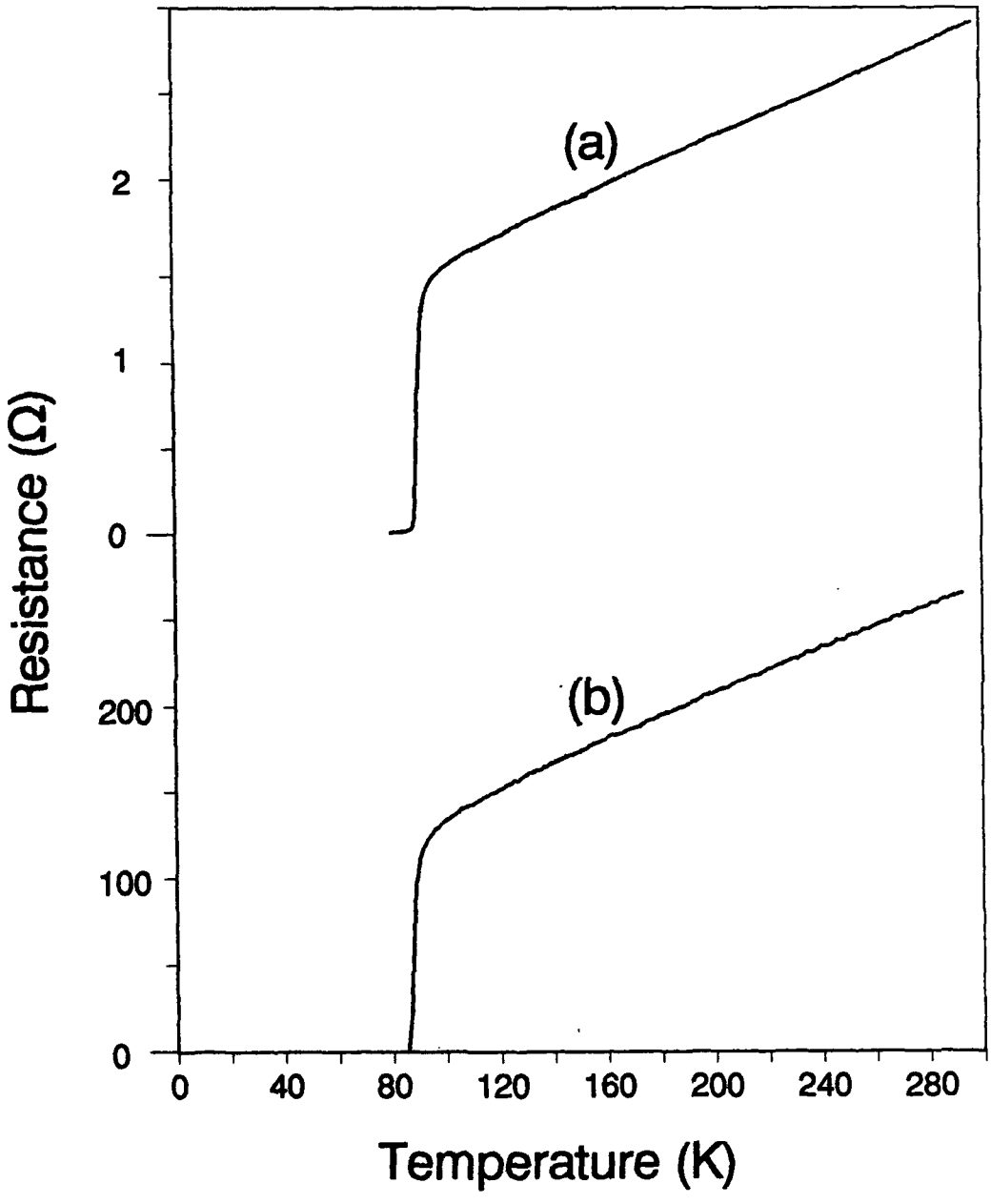
Figure 9



(a) (b)

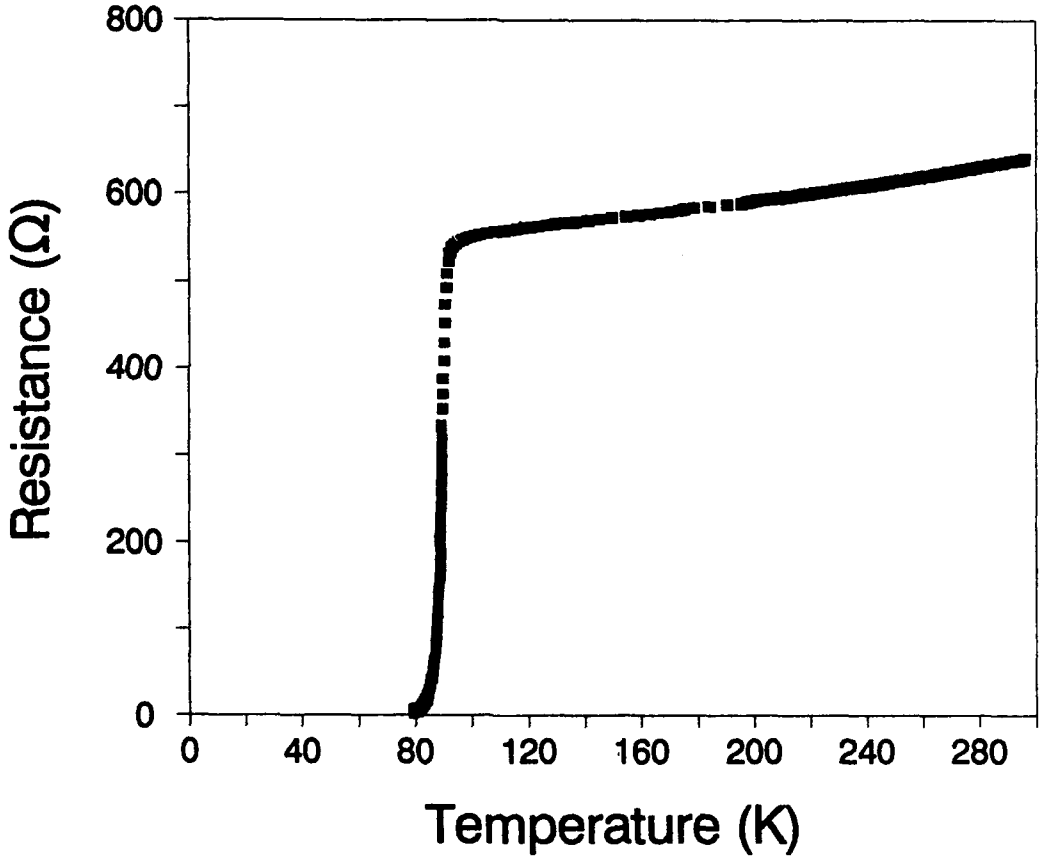
Micrographs of (a) a patterned Si film (bright) on a laser ablated YBCO film (dark) showing two 10 μm wide lines, and the same structures after the rapid thermal annealing of the sample at 970 °C for 30 s in oxygen.

Figure 10



Temperature-dependent resistance of two 10 μm wide, 200 μm long HTS line structure on a $SrTiO_3$ substrate. The lines were fabricated by reverse Si-YBCO reactive patterning technique.

Figure 11



Temperature-dependent resistance of two 10 μm wide, 200 μm long HTS line structure on a Si substrate with a MgO buffer layer patterned by the Si-YBCO reactive patterning technique.

Figure 12