ION AND PLASMA INDUCED PATTERNING OF $YBa_2Cu_3O_7$

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ABSTRACT

Thin films of the ceramic high temperature superconductor $YBa_2Cu_3O_7$ which had been deposited on $SrTiO_3$, $LaAlO_3$ and MgO substrates by dc sputtering in oxygen at pressures between 100 and 400 Pa with thickness between 100 and 500 nm, were patterned into narrow bridges by conventional photolithographic techniques followed either by reactive ion etching (RIE) in HCl or by chemically assisted ion beam etching (CAIBE) in Ar and HCl. Down to linewidths of 5 µm no reduction of the critical current densities was observed.

INTRODUCTION

Thin films of the high temperature superconducting material $YBa_2Cu_3O_7$ (YBCO) have gained wide interest because of their potential applications in microelectronics, high frequency techniques and magnetic field sensors. Such films may be deposited by laser ablation /1/, sputtering /2/ or (thermal or plasma enhanced) chemical vapour deposition /3/ and reach routinely values of the critical transport current density of more than 5×10^6 A/cm^2 /4/ and of the surface impedance of less than 40 mΩ at 86 GHz /5/, both at 77 K and zero magnetic field. Among the devices which have been realized until present are striplines /6/ with the aim of ultrafast (dispersion-free) inter-chip connects, transmission line resonators /7/ and filters /8/ for microwave applications, miniaturized microwave antennas /9/ which are under way of test for satellite communications, and SQUIDS /10/ with applications e.g. in medical systems.

In order to manufacture electronic devices, it is necessary to pattern YBCO films in the lower micrometer regime of linewidths. The main requests for an etch process are lack of damage to the superconducting film-properties, selectivity with respect to the process masks, to substrates like $SrTiO_3$, $LaAlO_3$, MgO, or $NdGaO_3$, and to buffer layers like yttrium stabilized zirconia (YSZ), a reasonable etch rate, low linewidth loss, and the potential of forming tapered edges.

Wet chemical etching generally suffers from underetching due to isotropy. Among the consequences are linewidth loss and undefined edges. In addition, for narrow bridges with linewidths below 15 µm etched into YBCO films of 300 - 400 nm thickness in 0.7 - 2 % H_3PO_4, we observed a reduction in j_c , which we attribute to a damage of the bridge edges down to a depth of several microns. The reason may be the penetration of the etching agent into the material along grain boundaries and the surface of precipitates.

Therefore there is obviously the necessity to develop dry-etching processes for such materials. Up to now, the substrate sizes are generally limited to one or two inch diameter, but it will be desirable in the near future to develop production dry-etching processes, that operate on larger substrate areas similar to those applied in silicon based microelectronics. Plasma and ion based techniques are supposed to be most powerful to fulfil these tasks, because they overcome the problems of inhomogeneity and throughput inherent to sequential writing techniques with focussed laser and ion beams.

PHYSICAL VERSUS CHEMICAL PATTERNING

Ion beam etching (IBE) with argon ions was extensively used for the patterning of YBCO /11/ and other high T_c superconductors as it was already under use for ferrites and garnets in memory technology. The etch rates in sputtered high quality YBCO-films that are obtained for an ion energy of 700 eV and a beam current density of 1.0 mA/cm^2 by this technique are 24 nm/min at an angle of incidence of 0° and 36 nm/min for 45°, the angle of maximum etch rate /4/. The 0° - values for photoresist (AZ 5218), and plates of the melt-grown single-crystalline substrate materials $SrTiO_3$, $LaAlO_3$, and MgO are 31, 20.3, 20.0, and 12 nm/min, respectively, from which the selectivities of YBCO with respect to these materials are calculated as 0.77, 1.2, 1.2, and 2.0. They are low except for MgO.

The way to overcome the low selectivities of pure physical etching is to employ a chemical component in order to either increase the etch rate of the YBCO or decrease the etch rate of the mask or substrate materials. The key to plasma-chemical etching is the formation of volatile end products and is widely used in semiconductor etching. There exist volatile organic compounds of Y, Ba and Cu, e.g. diketonates, which are used for chemical vapour deposition. In order to use them for dry etching, precursors for the formation of such compounds have to be found, which are stable in the plasma environment which is needed to achieve anisotropy.

In semiconductor etching, volatile halides are most frequently used to remove the etched material. The vapour pressures of the chlorides of the constituents of YBCO are higher than those of the fluorides, but they are, at 100 °C, still more than eight orders of magnitude lower than the one of $SiCl_4$. One possible way out of the problem associated with low volatility is to go to process temperatures of several hundred °C. The price to be paid is, that conventional photoresist can no longer be used as a process mask, and inorganic masks like Al_2O_3 or metals have to be employed instead. The inorganic masks are difficult to remove without residues. A second drawback of high temperatures ($\geq$ 400 °C) is the risk of irreversible degradation of the YBCO-films by oxygen loss.

An alternative approach is to etch at temperatures low enough ($\leq$ 120 °C) to allow for the use of resist masks, and to apply a strong physical etch component by ion bombardment in conjunction with chemically active species. In this process, which is generally referred to as chemically enhanced sputtering, an altered surface layer is formed which incorporates chemically active species that have either been adsorbed and mixed in by bombarding ions or implanted as reactive ions. An increase of the etch rate will occur, if the substrate atoms in this surface layer, have a lower binding energy than in the bulk material /12/. The selectivity of one material with respect to another can be increased by chemically enhanced sputtering, because the binding energies in the altered surface layers for both materials may differ from the corresponding bulk values to a different extent. It is difficult, to our knowledge, to predict the change in surface binding energies for different combinations of multicomponent materials and reactive species, because neither the exact composition of the surface layer nor the binding energies of the bulk materials are known.

We have therefore started to investigate experimentally CAIBE and RIE processes in HCl, in which both processes chemically enhanced sputtering is assumed to occur. In the first process ion bombardment by noble gas ions is combined with the adsorption of neutral halogen gas molecules and few beam-activated radicals to the surface, while in the second case beside neutral molecules many plasma-born radicals strike the surface, and among the impinging ions are reactive ones. Therefore the RIE situation is a much more complex one than that of CAIBE.

EXPERIMENTS AND RESULTS

Samples: The experiments on YBCO were performed with thin films, that had been deposited by high pressure dc-sputtering to thickness between 200 and 800 nm on $SrTiO_3$ or $LaAlO_3$ /4/. The films were single crystalline and highly c-axis oriented, and had critical current densities of more than 10^6 A/cm^2. The experiments on the substrate materials were carried out with cleaned substrates of the same type as were used for YBCO-film deposition. The circular $SrTiO_3$-samples had a typical diameter of 17 mm and a thickness of about 1 mm, while the $LaAlO_3$- and MgO-samples were squares of 10 × 10 mm with a thickness of 0.5 mm. All samples were single crystalline and oriented to within less than 1° to provide the c-oriented growth of YBCO.

Lithography: After cleaning of the surfaces of the YBCO-films in an oxygen plasma in a barrel-reactor, AZ 5214 or 5218 photoresist was spin-deposited on the samples. After a prebake in air at 80-90 °C patterns were transferred into the resist masks of 1.4 or 1.8 μm thickness by UV contact-printing photolithography. At the edges of the samples the resist formed a hump of a height of more than one micron, which limited the minimum distance between mask and surface and thereby the possible resolution of this technique to about 2 μm. After the development of the mask, a postbake in air was performed at 120 °C. Finally a short plasma treatment in oxygen was done to remove resist residues on the YBCO. The substrate-material samples were processed in a similar way.

CAIBE: The experiments were performed in an ion-milling machine (CSC Millatron VIII), which was equipped with a separate gas shower near the rotating sample stage. In order to mount the samples, they were attached to silicon wafers of 3" diameter by carbon adhesive. The wafers were then clamped onto the water-cooled chucks of the stage. A layer of metal-powder filled rubber between wafer and chuck guaranteed good thermal contact. The experiments were done under fixed beam-conditions of an ion energy of 700 eV and an ion-beam current density of 0.43 mA/cm^2. The current density had to be limited to this value to prevent the resist from thermal decomposition. Ar at a fixed flow rate of 2 ml_N/min was fed into the source of Kaufmann-type, while a variable flow of HCl was applied to the shower. Starting from the values for 0 ml_N/min HCl of 10.3, 7.3, 7.1 and 5.0 nm/min for YBCO, $SrTiO_3$, $LaAlO_3$ and MgO, the etch rates decreased drastically to 5.6, 2.8, 3.0 and 1.9 nm/min at an HCl-flow of 1 ml_N/min. In Fig. 1 the etch rates of different materials of interest normalized to their values at zero reactive gas flow are plotted as a function of reactive-gas flow.

The decrease of the measured etch rates may be due to three reasons. First, the increased pressure due to the HCl flow in front of the substrate will decelerate the Ar ion-beam and reduce its sputter-yield. Secondly, there may also be a reduction in beam current density due to increased scattering of Ar ions from HCl gas-molecules. Finally the sputter-yield may be decreased or increased by the presence of the chemically active species in the altered surface-layer, if they lead to an increased or decreased surface binding-energy of the metallic components.

At 1.5 ml_N/min HCl the etch rates increased again for $LaAlO_3$ and MgO, while it remained nearly constant for YBCO and decreased further to 2.2 nm/min for $SrTiO_3$, as compared to the values at 1.0 ml_N/min (Fig. 1). The reason for this behaviour may be, that at this HCl-flow, due to the higher coverage of the substrate surface by adsorbed HCl, chemical enhancement of the sputter-yield starts to overcompensate for the pressure-induced reduction of the etch rate, except for $SrTiO_3$. This would imply, that in contrast to the constituents of YBCO, $LaAlO_3$ and MgO, those of $SrTiO_3$ do not show a reduced binding energy in the chlorinated surface layer. Further experiments at higher HCl-flows have to confirm this assumption.

In Fig. 2 the ratio of the etch rates of YBCO and the substrate materials $LaAlO_3$, $SrTiO_3$ and MgO is plotted as a function of reactive-gas flow. MgO clearly had the highest selectivity of more than 2 over YBCO for low HCl-flows. It could be increased to approximately 3 at 1 ml_N/min. For $LaAlO_3$ no increase in selectivity as a function of reactive gas flow was observed, whereas for $SrTiO_3$ only for a flow of 1.5 ml_N/min an increase to about 2.7 was observed. From these results it is clear, that for $LaAlO_3$ no advantage of CAIBE with HCl over IBE is seen in the range of measured flows. For $SrTiO_3$ (1.5 ml_N/min) and MgO (1 ml_N/min) a single value of the HCl flow exists, where CAIBE has advantages over IBE in terms of selectivity. There the YBCO etch rate is about 60 % of that of the IBE rate, while the selectivities are twice and 1.5 times that of IBE, respectively.

RIE: The experiments were carried out in a parallel plate etcher (LH Z401) with grounded upper electrode and an interelectrode distance of 48 mm. The lower electrode was powered at 13.56 MHz by an rf generator, which also allowed for a measurement of the nominal power. The actual plasma power which is less due to losses in the connections and the matching network, was assumed to be proportional to the measured power. More details of the reactor are given in a recent work /13/.

The samples were located without clamping in the centre of the lower electrode, which was cooled by mineral oil and had a diameter of 150 mm. The pressure used in these experiments was 5 Pa at a flow rate of 10 ml_N/min. In Fig. 3 we show the power dependence of the etch rates of YBCO under these conditions in pure Ar and in pure HCl. The etch rates in HCl increase linearly with power from 1.6 to 6 nm/min between nominal power densities of 0.28 to 1.13 W/cm^2. These values are lower by a factor of two as compared to those published in literature /14/. The reasons are first the microloading effect of our resist mask as compared to the Al_2O_3-mask reported, and secondly the higher quality of the samples used in our etching experiment ($j_c \geq 10^6$ A/cm^2 at 77 K). We also observed higher etch rates on lower quality samples. The RIE etch rates are by about 50 % higher than the sputter-etch rates in Ar (Fig. 3). On the other hand the ion-current densities reaching the cathode may be different in the discharges in both gases, so that no conclusion on the chemical enhancement of the etching process by chemically active species can be drawn from this result.

Critical Current Densities: The critical current densities were measured on microbridges of 200 µm length and a width between 5 and 50 µm, which had been dry etched. A voltage criterion of 10 mV /cm was applied. No degradation of j_c could be observed in the bridges down to 5 µm width. This behaviour is clearly better than the one observed in wet etching.

CONCLUSIONS

The ion and plasma induced dry etching methods CAIBE and RIE using HCl may be employed with conventional resist lithography to pattern YBCO in the lower micron range. The damage to the superconducting properties of the films is lower than for wet chemical etching. The selectivity of CAIBE with respect to substrates of $SrTiO_3$ and MgO can be increased to 2 and 1.5 times the values observed in Ar ion milling, but at the cost of a reduced etch rate of YBCO. In contrast, no effect on the selectivity of YBCO over $LaAlO_3$ is observed.

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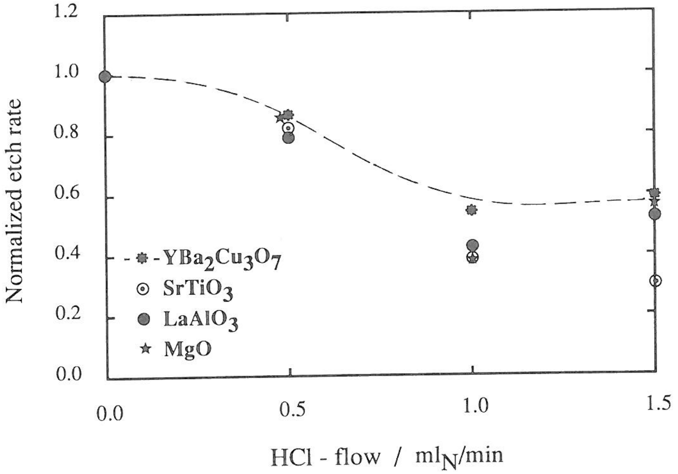

Figure 1: CAIBE etch-rates for YBCO and three substrate-materials as a function of the HCl reactive-gas flow, normalized to their values for zero flow; the Ar^+ ion-beam had an energy of 700 eV and a current density of 0.43 mA/cm^2.

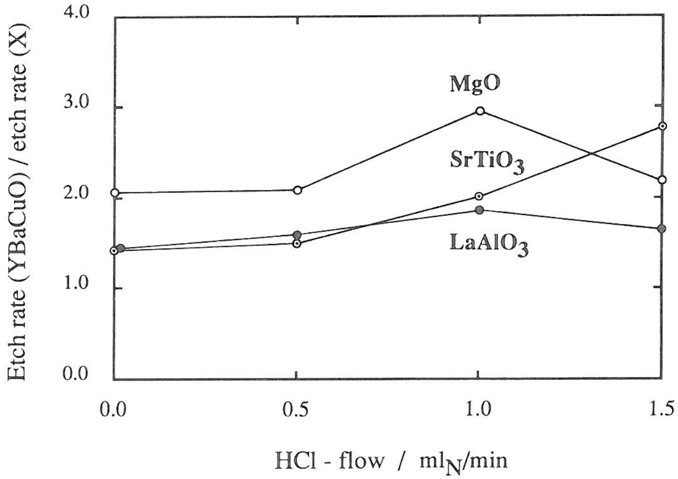

Figure 2: Ratio of the CAIBE etch-rates of YBCO and three substrate-materials (selectivity) as a function of the HCl reactive-gas flow; the Ar^+ ion-beam had an energy of 700 eV and a current density of 0.43 mA/cm^2.

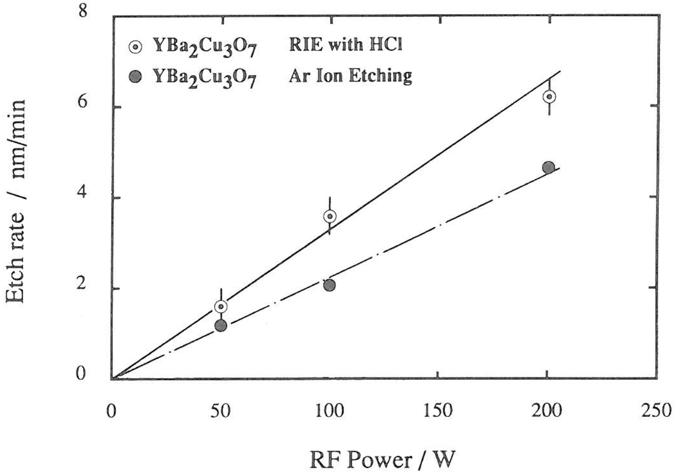

Figure 3: RIE etch-rates and sputter etch-rates of YBCO thin-films in HCl and Ar, as a function of the nominal discharge power, measured at the generator output; the discharge-conditions in both sets of experiments were: electrode separation 48 mm, powered lower electrode; electrode diameter 150 mm; frequency 13.56 MHz; pressure 5 Pa; gas flow-rate 10 ml$_N$/min.