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# High-T$_{\text{c}}$ Superconductors Tailored on the Nanometre-Scale

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# High-$T_c$ superconductors tailored on the nanometre-scale

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High-$T_c$ superconductors are characterized by an unusually small coherence length, which amounts to a few ångströms only. As the coherence length is the length scale in which a superconductor has to be structured to achieve Josephson junction behaviour, considerable effort has been devoted by many groups to modify high-$T_c$ films in the nanometre scale. Because the high-$T_c$ cuprates do not lend themselves for nanostructuring, new concepts have to be developed to achieve this goal. These developments will be discussed and an overview of the state of the art of the field will be presented with a special focus on the ultimate limitations of nanoscale structuring of superconductors.

## 1. Introduction

There are three fundamental length scales intrinsic to a superconductor (see figure 1): the atomic distances, the superconducting coherence length and the magnetic penetration depth.

The atomic distances, or analogously the lattice constants, are usually the smallest lengths. They present the ultimate limit for the attainable feature size for patterning, but do not impose a limit for vertical structuring, as new high-$T_c$ materials can be fabricated by utilizing controlled layered growth on a sub-unit-cell level.

The second length of fundamental importance is the coherence length $\xi$ of the superconducting order parameter. The coherence length can be imagined naively as the diameter of the Cooper pairs, but strictly speaking, it is the minimum length over which the superconducting order parameter, which is proportional to the critical temperature $T_c$ of the superconductor, can be changed significantly. Consequently, if a superconducting bridge is so small that its dimensions are comparable to the coherence length, it cannot behave as a strong superconducting link, but will be a Josephson junction (see figure 2*a*). As sketched in figure 1, the coherence length increases as a function of temperature, and diverges at $T_c$ according to

$$\xi(T) \propto (1 - T/T_c)^{-1/2}. \qquad (1.1)$$

But because $\xi(T)$ increases rather slowly at low temperatures, $\xi(0)$ can be used as a meaningful reference value for a wide temperature range. In high-temperature superconductors, the coherence length is anisotropic and extremely small. For example, for $YBa_2Cu_3O_{7-x}$ (see figure 3), a working horse among the high-temperature superconductors, the coherence length $\xi(0) \approx 15$ Å along the CuO-planes and about 1.5–3 Å perpendicular to them. For comparison: Nb and Pb, two classical low-temperature

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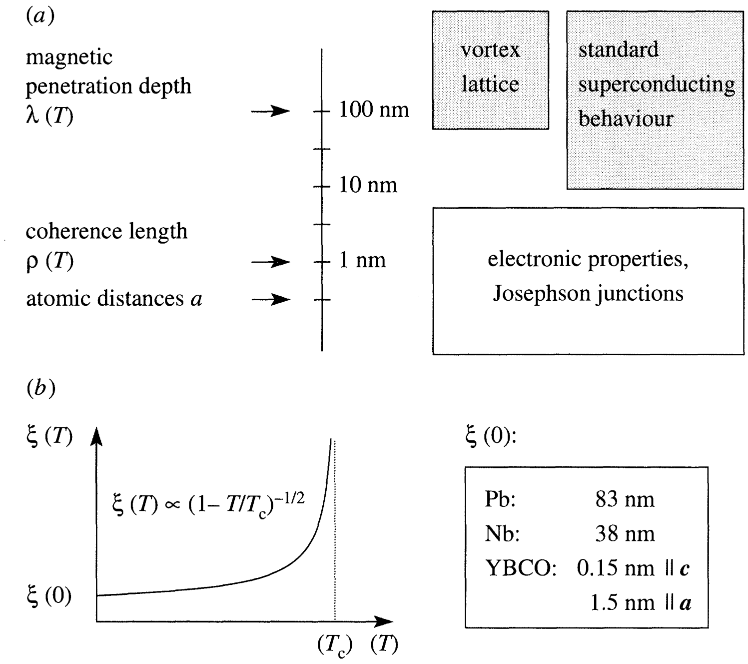

Figure 1. (*a*) Illustration of the fundamental length scales in high-$T_c$ superconductors; (*b*) sketch of the temperature dependence of the superconducting coherence length $\xi(T)$. The concept of this figure originated from a viewgraph shown by M. Beasley at the symposium 'layered Superconductors: Fabrication, Properties and Applications, MRS Spring Meeting, 27 April–1 May 1992, San Francisco, USA.

superconductors, have coherence lengths $\xi(0)$ of 380 Å and 830 Å, respectively. As far as nanostructuring is concerned, the coherence length has two important implications: first, a superconductor can only be used in the conventional sense for current transport down to the feature sizes of the order of the coherence length. Second, to fabricate nanobridge-type Josephson junctions, one needs to pattern the superconductor with a resolution comparable to the coherence length, which obviously poses a challenge in the case of high-$T_c$ materials.

The third length scale, being for all practical materials the largest one, is the magnetic penetration depth. It describes the diameter of the magnetic flux lines in the superconductor. For high-$T_c$ superconductors it equals about 100–500 nm and is thus only of marginal interest in the context of nanostructuring.

The efforts to nanostructure high-$T_c$ superconductors concentrate on two types of devices: superconducting interconnects (figure 4) and Josephson junctions (figure 2). After discussing these devices in the following, several ingenious techniques will be presented that have been developed in the last few years with the objective of structuring high-$T_c$ films at the smallest scale possible.

## 2. Superconducting interconnects

Compared to normal metal lines, three basic advantages make superconducting interconnects attractive: they can be operated with negligible loss, dispersion is insignificant, and they can carry outstanding current densities. For example, in standard epitaxial films of $YBa_2Cu_3O_{7-x}$, supercurrents can flow with densities of *ca.*

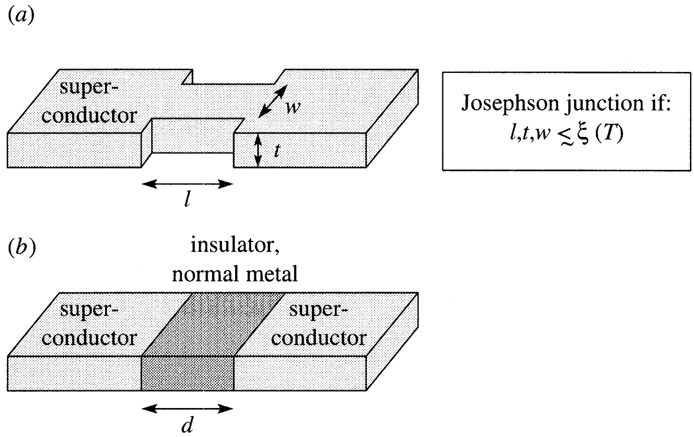

Figure 2. Sketch of the two types of Josephson junctions: (*a*) nanobridge-type junction and (*b*) barrier-type junction.

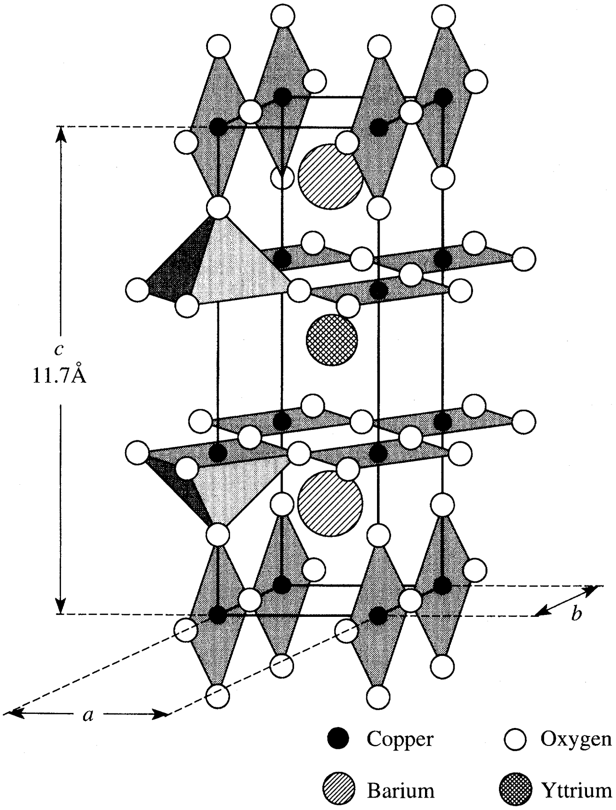

Figure 3. Unit cell of $YBa_2Cu_3O_7$.

$5 \times 10^7$ A cm$^{-2}$ at 4.2 K and of $5 \times 10^6$ A cm$^{-2}$ at 77 K, to be compared with *ca.* $4 \times 10^5$ A cm$^{-2}$ for today's interconnents in VLSI circuits. The higher current density available can be directly turned into a higher packaging density, if patterning can be done with adequate resolution.

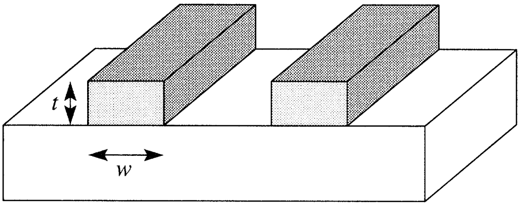

Figure 4. Cross-sectional sketch of two interconnects.

The ultimate limits for lateral nanopatterning of standard $c$-axis-oriented high $T_c$ lines made of $YBa_2Cu_3O_{7-x}$ are given approximately by the coherence length $\xi_{ab} \approx 15$ Å, and in the vertical direction by the unit cell size of about 12 Å.

Superconducting interconnects with widths in the range of 200 nm have been prepared by several groups using Ga ion-beam etching (Zaquine *et al.* 1992; Jiang *et al.* 1991; Barth *et al.* 1993). Some of these groups (but not all) reported astounding increases of the critical current densities with decreasing linewidths $w$ to values well above $10^8$ A cm$^{-2}$ at 77 K for $w \leqslant 200$ nm.

A technique for patterning high-$T_c$ superconductors, which exploits a peculiarity of these materials, is direct laser writing (Sobelewski *et al.* 1994). It relies on the fact that in the high-$T_c$ cuprates, $T_c$ is a function of oxygen content. For $YBa_2Cu_3O_{7-x}$, for example, $T_c$ is reduced from 93 K to 0 if the sample is reduced to $YBa_2Cu_3O_{6.4}$.

This behaviour can be exploited for patterning samples by scanning the surface of oxidized superconducting films in a $N_2$ atmosphere with a focused laser beam. As soon as $YBa_2Cu_3O_{7-x}$ is heated above 400 °C, oxygen diffuses out of the film. As the film surface is heated in the beam focus, the film gets locally reduced and turns insulating. Reversing the procedure is also possible: superconducting lines can be written by laser heating a reduced non-superconducting film in an $O_2$ atmosphere. The smallest feature size published today is 4 μm (Sobelewski *et al.* 1994), the ultimate limit of resolution given by the laser wavelength and by the thermal healing length of the film. Thus, the resolution may be increased substantially if the stoichiometry of the superconductor can be disturbed by an AFM/STM-based technique (Heinzelmann *et al.* 1988; Thomson *et al.* 1994).

## 3. Josephson junctions

Josephson junctions can be classified into nanobridge-type and barrier-type junctions, as sketched in figure 2. Both types require structuring on the nanometre scale, as will be discussed in the following.

### (*a*) *Nanobridge junctions*

Nanobridge junctions have been prepared successfully by a number of groups using electron beam lithography and chemical ion beam etching. In the best cases, bridges as small as 20 nm$^3$ were obtained (Martens *et al.* 1993, 1994; Wendt 1992; Schneider *et al.* 1993; de Nivelle *et al.* 1993). Nanobridge junctions have been already incorporated into devices like superconducting flux flow transistors (Schneider *et al.* 1993) or superconducting quantum interference devices. In one (unconfirmed) report, even a 32-bit shift register composed of more than 60 nanobridges and working at 120 GHz (77 K), is described (Martens *et al.* 1994).

A device size of 20 nm$^3$ is outstanding for any type of electronic circuit, and is not far away from the ultimate limit for superconducting devices. Although, in principal,

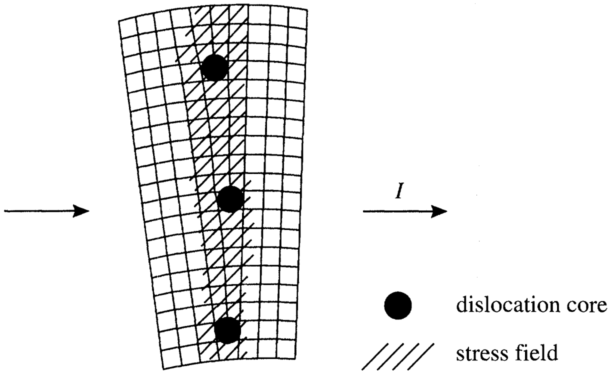

Figure 5. Sketch of a low angle grain boundary ((001) tilt) in an high-$T_c$ film. An array of edge dislocation is formed at the boundary, which, together with a mechanical stressed zone of few nanometre width, acts as a Josephson junction.

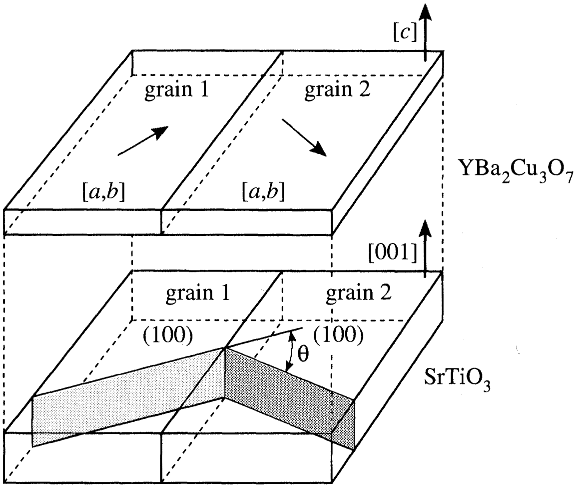

Figure 6. Illustration of the bicrystal-technique used to grow high-$T_c$ films with single well defined grain boundaries. As shown, the high-$T_c$ film is grown epitaxially on a bicrystalline substrate (Tsuei *et al.* 1989).

the length can be further reduced to the coherence length of 0.15–1.5 nm (depending on film orientation), there is a strict requirement on the cross section of $w \times t$ of the bridge imposed by thermal fluctuations: a Josephson junction operates by coupling the two order parameters of the superconducting banks adjacent to the nanobridge. The coupling energy $E_J$ is proportional to the maximum supercurrent (the so-called critical current) $I_c$ of the junction: $E_J = I_c/h2e$. As $E_J$ has to be larger than $kT$, a requirement on $I_c$ is derived: $I_c > 20\ \mu A$ (77 K), and $I_c > 0.5\ \mu A$ (4.2 K). Thus, for a critical current density of $5 \times 10^6\ A\ cm^{-2}$ at 77 K and of $5 \times 10^7\ A\ cm^{-2}$ at 4.2 K, the product $tw$ has to be larger than 200 nm$^2$ at 77 K and than 1 nm$^2$ at 4.2 K.

### (*b*) *Barrier-type junctions*

In a barrier-type junction, a well superconducting bridge is interrupted by a thin barrier layer of a different material, which may be an insulator, semiconductor, normal metal, or even a superconductor with a low-$T_c$ (figure 2*b*). As this layer has to be rather thin, of the order of a few multiples of the decay length of the super-

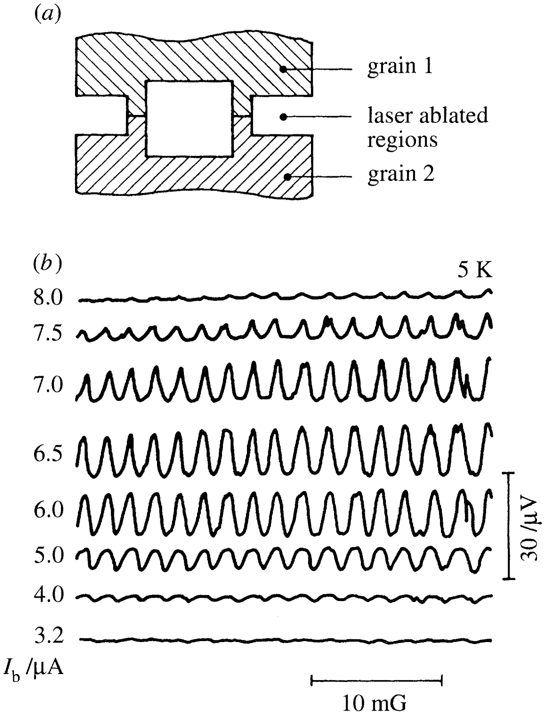

Figure 7. (*a*) Illustration of a superconducting quantum interference device (SQUID) in which one grain boundary is used as a Josephson junction. (*b*) Voltage drop across the SQUID as a function of applied magnetic field for a range of bias currents (Tsuei 1989).

conducting wavefunction in the barrier material only, structuring to a feature size of a few nanometres, or a few tens of nanometres, is also required for this type of Josephson junction. There has been an immense effort to fabricate such structures by means of multilayer growth (see, for example, Weinstock & Ralston 1993). As this approach relies on rather standard techniques of thin film growth, it will not be discussed in further detail. Instead, we will show how ultrathin barriers have been obtained within a single layer film.

### (i) *Grain boundary junctions*

The coherence length of the high-$T_c$ cuprates is so small that in these superconductors even single grain boundaries, which have a width of the order 1–10 nm, can be used as high-quality Josephson junctions (Dimos *et al.* 1994). Therefore, a number of techniques have been developed to fabricate high-$T_c$ films with well defined grain boundaries at desired locations. These techniques include epitaxial growth of high-$T_c$ films on bicrystalline and multicrystalline substrates (see figure 6) (Dimos *et al.* 1990), film growth on substrate with steps (Dilorio *et al.* 1991; Siegal *et al.* 1993), or on substrates which are partly covered with seed layers to induce misoriented growth (Char *et al.* 1991).

Single grain boundaries have been successfully employed for device fabrication; in particular, for the fabrication of SQUIDs. Figure 7 shows data of one of the first single grain boundary SQUIDs; in this figure the SQUID oscillations are clearly visible.

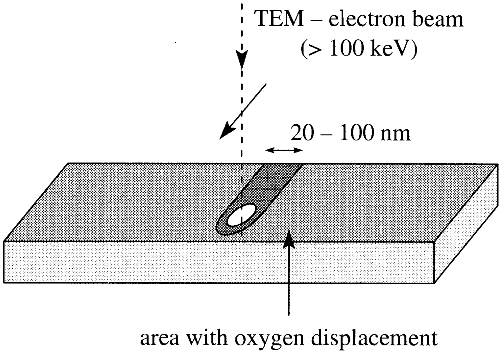

Figure 8. Illustration of the direct writing technique used to produce narrow non-superconducting barriers in a superconducting line by scanning the electron beam of a scanning transmission electron microscope over the sample surface.

### (ii) *Josephson junctions made by direct electron beam irradiation*

If $YBa_2Cu_3O_{7-x}$ films are irradiated by an electron beam with an energy larger than about 80 keV, the impinging electrons disorder the ions of the film, moving in particular the oxygen. The disordered zone created in this way is rather small; diameters as low as 20 nm have been measured. Therefore, a Josephson junction can be fabricated by scanning, with the electron beam of a scanning transmission electron microscope, a barrier into a superconducting line, as sketched in figure 8 (Pauza *et al.* 1993; Tolpygo *et al.* 1993). Obviously, this technique can also be used for the fabrication of nanobridges. Barrier-type Josephson junctions fabricated this way have excellent properties, and, due to their flat surface, are well suited for integration in multilayer structures.

## 4. Patterning by STM/AFM

Very early after the discovery of high-$T_c$ superconductivity, it was noticed (Heinzelmann *et al.* 1988) that the (001) surface of bulk single crystals could be modified by using scanning tunnelling microscopy. By applying a sample bias voltage of 4 V with a tunnelling current of 10 nA of 5 s, which led to an instability of the feedback circuitry, Heinzelmann and co-workers (1988) were able to produce apparent holes in the (001) surface of $HoBa_2Cu_3O_{7-x}$. These holes had a diameter of only 10–80 nm, and, immediately after their formation, a depth of about 40 nm. The features filled in slowly, and after 15 min their depth reduced to about 4 nm. This suggests that the holes do not represent topographic modifications of the sample surface but rather result from changes in the sample conductivity, due to changes in the oxygen stoichiometry induced by the scanning tunnelling process. Doing similar experiments, again at room temperature and in air, real etch processes were noticed for $Tl_2Ba_2CuO_{6+x}$ (Parks *et al.* 1991) and for $YBa_2Cu_3O_{7-x}$ (Thomson *et al.* 1994; Heyvaert *et al.* 1992). Furthermore, the (001) surface of $YBa_2Cu_3O_{7-x}$-films can be milled mechanically by scanning an STM-tip (Thomson *et al.* 1994) or an AFM-tip across the film surface (Ch. Gerber *et al.* 1994, unpublished work). In addition, Thomson and coworkers (1994) showed that $YBa_2Cu_3O_{7-x}$ films can structured with an STM by thermal heating and by electrochemical etching. Taken together, these experiments clearly demonstrate the possibility of patterning high-$T_c$ materials in the nanometre scale by STM/AFM techniques. Nevertheless, it seems as if these techniques have not yet been utilized for the fabrication of interconnects or of nanobridges.

## 5. Summary

Due to their small coherence lengths, the high-$T_c$ cuprates can be used as superconducting interconnects with widths of a few tens of nanometres, or as Josephson junctions with a surface area of a few hundred square nanometre. Therefore, nanopatterning of these materials is an attractive undertaking, pursued by a number of groups. Structuring high-$T_c$ materials on the nanometre scale has been demonstrated by applying known technologies to the high-$T_c$ compounds, like ion-beam etching, STM-etching or AFM-milling. But the challenge of fabricating nanometre-sized patterns in the high-$T_c$ cuprates has also led to the development of new and original technologies; for example, the direct electron beam writing of Josephson junctions or by various techniques to engineer grain boundaries.

It was the purpose of this paper to present these developments to an audience outside the field of superconductivity, which hopefully may find some of them inspiring for their future work.

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