Masked ion beam irradiation of high-temperature superconductors: patterning of nano-size regions with high point-defect density

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Abstract: Ion-beam irradiation of high-temperature superconductors creates different types of defects depending on ion mass, energy and dose. Computer simulations reveal the diversity of the ion-target interactions with \(\text{YBa}_2\text{Cu}_3\text{O}_7\) and are compared to previous experimental results from transmission electron microscopy and electrical transport properties. While protons have a very low efficiency to create defects in \(\text{YBa}_2\text{Cu}_3\text{O}_7\), significantly heavier ions produce defect clusters and inhomogeneous damage in the target material. The situation is exemplarily illustrated by a computer simulation study of the defect cascades produced by \(\text{H}^+, \text{He}^+, \text{Ne}^+\), and \(\text{Pb}^+\) ions of moderate energy. \(\text{He}^+\) ions with energy of about 75 keV were found useful for a systematic modification of the electrical properties of high-temperature superconductors, since they do not implant into 100-nm thick films of \(\text{YBa}_2\text{Cu}_3\text{O}_7\) but primarily create point defects by displacement of the oxygen atoms. Such defects are very small and distributed homogeneously in \(\text{YBa}_2\text{Cu}_3\text{O}_7\). The small lateral spread of the collision cascades allows for the patterning of nanostructures by directing a low-divergence beam of \(\text{He}^+\) ions onto a thin film of \(\text{YBa}_2\text{Cu}_3\text{O}_7\) through a mask. Simulations indicate that the resolution can be about 10 nm. An experimental test with a masked ion beam irradiation confirmed that features with about 200 nm size could be produced in a \(\text{YBa}_2\text{Cu}_3\text{O}_7\) thin film and observed by scanning electron microscopy.

Keywords: high-temperature superconductors; nanopatterning; masked ion irradiational; point defects; electrical resistivity; Hall effect.


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1 Introduction

Nanodevices made of superconductors would offer many advantages for novel technologies. The most evident one is a reduction of heat dissipation that is a severe obstacle for the ongoing down-scaling trend in electronic circuits. Although superconductive electronic circuits have been successfully demonstrated with classical superconductors [1], the use of the novel high-temperature superconductors (HTS) with their much more practical cooling requirements would result in a clear advantage on the market. Unfortunately, the well-established lithography technologies from semiconductor manufacturing, that can be applied – with some modifications – to metallic superconductors, are not suitable for creating high-resolution structures in HTS.

For the fabrication of novel devices based on high-temperature superconducting thin films, systematic tailoring of electrical properties is desirable, in particular if it can be done on a length scale of few nanometres. This would open the possibility to create fundamental elements of superconducting electronics, like the Josephson junction. Using ion irradiation for this task has been proposed some time ago, but research activities have been focused mainly on the creation of columnar defects by high-energetic
heavy ions [2]. Such severe defects are important for the enhancement of the critical current in HTS that is of primordial technical importance for the fabrication of superconducting cables with high current-carrying performance but are not suited for a homogeneous modification of the electrical properties of a HTS. In the following, we will investigate how this is changed by using ions with rather small mass and moderate energy.

2 Creation of defects by ion irradiation

The microscopic impact of ion irradiation is hardly directly experimentally accessible but computer simulations of atomic collision cascades is a well established technique to predict the damage effects of various ion species in a wide range of energies. We have used two standard algorithms, the programs SRIM/TRIM [3] and MARLOWE [4] and have found a mutually good agreement of the results. Both methods are based on the binary collision approximation and include quantum-mechanical treatment. Whereas SRIM assumes an amorphous target and a Monte-Carlo method for the evaluation of the scattering cascades, MARLOWE provides a more detailed assessment of the ion-induced damage on the basis of the target’s crystalline structure. We have performed the computer simulations with parameters that correspond to our experimental investigations discussed later, i.e., a 100 nm thick film of YBa$_2$Cu$_3$O$_7$ (YBCO) on MgO substrate. Several different ion species, like H$^+$, He$^+$, Ne$^+$, and Pb$^+$ have been analysed in the simulations. The impact of different ions is visualised in Figures 1 and 2, respectively.

In the case of H$^+$ ions with 75 keV energy, very little interaction with the target atoms takes place and, consequently, a very high dose would be needed to produce a significant amount of defects in the HTS film (Figure 1, left panel). An advantage of proton irradiation is that the ions are little deflected from their incidence direction during traversing the target. Such a small lateral spread is demanded for preparing nanostructures in thin HTS films by ion damage. The impact of 75 keV He$^+$ ions on YBCO is shown in the right panel of Figure 2. The number of defects created in YBCO is significantly larger as compared to protons and the lateral spread is about ±10 nm when the ions exit at the backside of the YBCO film. Irradiation with only moderately heavier ions changes the picture dramatically. Ne$^+$ projectiles, as displayed in the left panel of Figure 2, are strongly deflected from their incidence direction. They cause a large number of defects, in particular also many displacements of the heavier atoms Y and Ba. The large number of defects per crystallographic unit cell presumably leads to a breakdown of the crystal structure and to amorphisation of the target material. Even more pronounced is the impact of heavy Pb$^+$ ions with 75 keV energy, shown in the right panel of Figure 2. The energy of the ions is exhausted after an average penetration depth of about 30 nm and they are implanted into the target material. As will be discussed later, full penetration of the ions through the superconducting film is necessary to pattern structures into the HTS film. In principle, it is possible to accelerate heavy ions to higher velocities to achieve full penetration but this leads to the creation of the above-mentioned columnar damage tracks.
Figure 1 Scattering cascades of target atoms in a 100 nm thick YBCO film after irradiation with 100 H\(^+\) ions (left panel) and 100 He\(^+\) ions (right panel). The ion’s direction of incidence is marked by the arrow. Light grey dots correspond to displaced oxygen atoms, darker shadings mark the heavier elements Cu, Y, Ba.

Figure 2 (Left panel) Scattering cascades of target atoms in a 100 nm thick YBCO film after irradiation with 100 Ne\(^+\) ions. Defects are created far off the ion’s direction of incidence. As for H\(^+\) and He\(^+\), the majority of ions are not implanted in the YBCO film. (Right panel) Scattering cascades of target atoms in a 100 nm thick YBCO film after irradiation with 100 Pb\(^+\) ions. The heavy Pb\(^+\) ions cannot penetrate through the film and implant into the YBCO thin film, creating many defects.

From these simulation results it is obvious that a change of the electrical and superconducting properties of YBCO might be expected not only for heavy ion irradiation, but, in a less dramatic fashion, also for the light ions. Several previous experimental studies have investigated the impact of ions with low or moderate mass on YBCO thin films. For Be\(^+\), Ne\(^+\), and Ar\(^+\) ions of energies ranging between 1 MeV and 3.5 MeV a pronounced increase of the resistivity and a reduction of the critical temperature $T_c$ was observed [5]. The superconducting transition becomes significantly broader after irradiation. Ion beam induced defects that cluster into small (<10 nm) disordered areas were detected. The size and density of these possibly insulating regions increase with the ion fluence. Another work reports the creation of amorphous zones after irradiation with 500 keV O\(^+\) ions [6]. In the isostructural compound GdBa\(_2\)Cu\(_3\)O\(_7\) stable amorphous areas that aggregate and overlap with increasing dose after irradiation with 300 keV Ne\(^+\) and 100 keV Xe\(^+\) ions were found in HREM investigations [7].
A comparative study of the irradiation of YBCO thin films with either 300 keV protons or 600 keV Ar\(^+\) ions indicated different defect structures that were attributed to displaced oxygen atoms in the former and the overlap of insulating regions in the latter case, respectively [8]. Proton irradiation leads to small defects that are statistically distributed in the material, but the complete suppression of superconductivity in YBCO requires a dose of the order of several \(10^{16}\text{ cm}^{-2}\) that might be prohibitive for practical applications. Such behaviour confirms the results presented in Figure 1. Irradiation of YBCO with 50 keV or 130 keV He\(^+\) results in an orthogonal to tetragonal transition of the crystal lattice due to oxygen displacement at a dose of about \(5 \times 10^{15}\text{ cm}^{-2}\), but no extended defect clusters can be detected in TEM investigations below this threshold [9]. However, irradiation defects manifest themselves in an increase of the normal state resistivity and a reduction of \(T_c\) at ion fluence even below \(10^{15}\text{ cm}^{-2}\) [10].

Our experiments were performed by irradiation of YBCO films with a typical thickness of about 100 nm with 75 keV He\(^+\) ions. Details about the experimental procedures can be found in Lang et al. [11]. The left panel of Figure 3 shows an exponential resistivity increase with the cumulative ion fluence at both room temperature (300 K) and at 100 K. The resistivity at 100 K is increased by about two orders of magnitude upon irradiation with a fluence of \(5 \times 10^{15}\text{ cm}^{-2}\). Remarkably, the superconducting transition remains sharp, indicating an intrinsic change of the electronic properties of the material, rather than a creation of non-superconducting clusters [11]. A dose of \(3 \times 10^{15}\text{ cm}^{-2}\) marks the crossover from superconducting material with a metallic-like temperature dependence to a semiconducting temperature behaviour (Figure 3, left panel) and the suppression of superconductivity (Figure 3, right panel).

**Figure 3** (Left panel) Resistivity increase at 100 K and 300 K as a function of the cumulative fluence in the normal state of an YBCO film after irradiation with 75 keV He\(^+\) ions. (Right panel) Decrease of the critical temperature \(T_c\) of the YBCO film after ion irradiation. \(T_c\) is defined by the midpoint of the superconducting transition. Lines are guides to the eye.

With an irradiation dose below \(2 \times 10^{15}\text{ cm}^{-2}\) the linear resistivity vs. temperature behaviour in the normal state, that is characteristic for optimally-doped YBCO, is preserved. The slope remains the same, but the resistivity offset extrapolated to \(T = 0\) K increases with the ion dose. Hall effect measurements revealed that the carrier mobility is systematically decreased with the irradiation dose. These results indicate that the
number of mobile carriers remains unchanged, but the number of defects is increased with the irradiation dose and the defects act as scattering centres [11]. Although a similar suppression of superconductivity can be achieved by oxygen-depletion in YBCO [12], the temperature dependencies of resistivity and Hall effect are different from those observed after ion irradiation. The electrical measurements together with the microscopic investigations imply that He⁺ irradiation of YBCO at energies less than 100 keV creates homogeneously distributed point defects via oxygen displacements.

3 Nano-structures by masked ion beam irradiation

Common techniques for the patterning of HTS films are chemical etching or ion milling, where the structures are defined by a layer of photoresist on top of the HTS. This causes underetching and unfavourable chemical reactions during the process and results in the formation of a textured surface that is a major disadvantage for growing additional epitaxial layers of HTS, a protection layer, or other material. Strain on the edges of the patterned film and the wavelength of the light used for exposing the photoresist limit the minimum size of device structures. In addition, such techniques involve several processing steps even for the fabrication of a simple circuit like a superconducting connecting line between two devices.

Josephson junctions in HTS have been only demonstrated with rather complicated and time-consuming production methods. Bicrystal grain boundary junctions [13], edge-type junctions [14], and ion-beam damage junctions have been reported. Also in the latter case several production steps were necessary: Either a layer of photoresist was processed by focused ion beam [15] or standard UV lithography [16] and then etched, or a metal mask was directly deposited on the YBCO film and then patterned by ion beam milling [17,18]. In a final step, the HTS was ion irradiated through the resulting trench.

The reproducible and systematic change of the electrical properties of HTS by irradiation with He⁺ ions of moderate energy, as discussed above, can be used for the novel method Masked Ion Beam Direct Structuring (MIBS) of HTS that is schematically shown in the left panel of Figure 4. A film of a HTS is prepared on a suitable substrate with a thickness small enough that the ions of the selected energy can penetrate through this film and implantation is avoided. A mask is placed at small distance from the film and protects selected areas of the HTS film from being irradiated. After subjecting the arrangement to an ion beam with large cross section and very low beam divergence, selected parts of the film are converted to non-superconducting, where those regions protected by the mask pattern remain superconducting. The major advantage of such single-step technique is the direct, non-contact structuring of superconducting devices with a resolution that is essentially only limited by the masking technique. It does not require the multiple processing steps connected with the use of photoresist and avoids possible surface degradations. The large ion-beam exposure fields would enable the processing of many structures in parallel.

For a practical realisation of MIBS it is crucial to investigate the possible lateral resolution of this technique. A simulation of the lateral spread of the collision cascades and the homogeneity of defect generation along the thickness of the film is presented in
the right panel of Figure 4. The irradiation is applied through a mask with a 50 × 50 nm² hole and it is assumed that the ion beam has no divergence. The defect area laterally widens to about 60 × 60 nm² at the bottom of the YBCO film, which indicates that irradiation with He⁺ through a mask should achieve a principal resolution of about 10 nm. Close inspection of Figure 4, right panel, shows that preferentially the oxygen atoms in the YBCO crystal structure are displaced, whereas the impact on the heavier atoms is significantly lower, in accordance with the microscopic results [9]. The atoms are displaced by a short distance only, typically at the order of the size of a unit cell. This is a further indication that no loss of oxygen from the YBCO has to be expected.

Figure 4 (Left panel) The principle of masked ion beam direct structuring (MIBS) of HTS. A mask with the particular pattern is placed at small distance above a superconducting film prepared on a substrate. The pattern can be projected to the HTS film in a 1 : 1 reproduction with a large exposure field. (Right panel) Computer simulation of the ion-beam induced defects with the program MARLOWE. A 100 nm thick film of YBa₂Cu₃O₇ is irradiated with 75 keV He⁺ ions through a mask with a 50 × 50 nm² hole, at a dose of 1 × 10¹⁴ cm⁻². Target atoms that are displaced are indicated by their original (open symbols) and stopping positions (full symbols).

For experimental patterning tests epitaxial films of YBCO with thicknesses of the order of 100 nm were fabricated on (100) MgO substrates by pulsed laser deposition [19]. A silicon stencil mask with various test patterns and features in the dimensions from about 50 nm to 1.5 µm was placed on top of the YBCO film according to the arrangement presented in the left panel of Figure 4 and irradiated with 75 keV He⁺ ions. Arrays of ion-irradiated regions were created in the YBCO film, corresponding to the holes in the mask and investigated by scanning electron microscopy (SEM), where dark regions correspond to the irradiated areas. As an example, a periodic pattern of irradiated dots is shown in Figure 5. The contrast in the SEM picture results presumably from the different electronic work functions of regions with different conductivity. The irradiated areas have a diameter of about 200 nm and the edges are well defined. Further experiments with different masks indicated that even significantly smaller features might be possible with this technique.

In summary, irradiation of YBCO by He⁺ ions of moderate energy together with appropriate masking techniques may provide an effective tool to pattern superconducting structures and devices on a nano-scale in a single processing step.
Masked ion beam irradiation of high-temperature superconductors

Figure 5 Scanning electron microscopy (secondary electron detection) picture of a thin YBCO film after He⁺ ion irradiation through a silicon stencil mask. The dark regions correspond to the areas that were irradiated through mask holes of about 200 nm diameter.

Acknowledgements

This work was supported by the Austrian Science Fund (FWF), the Micro@Nanofabrication Austria (MNA) Network, funded by the Austrian Federal Ministry for Economic Affairs and Labour, and the European Science Foundation program Nanoscience and Engineering of Superconductors (NES).

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