High oxygen pressure deposition and patterning methods for metal oxide heterostructures

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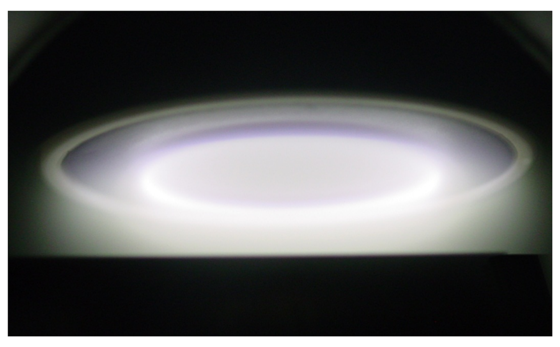
Abstract

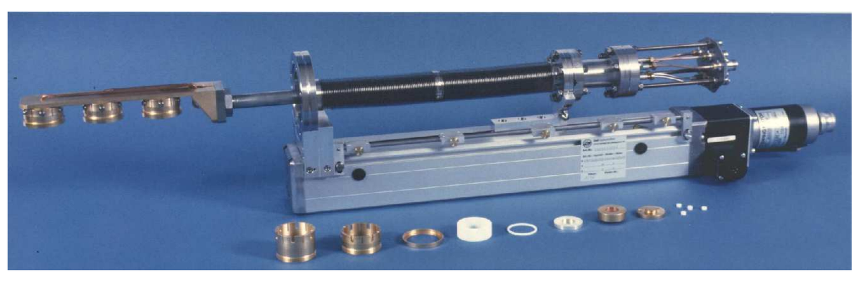
Significant technological efforts are required to produce high-quality samples of superconducting cuprates due to their sensitivity to the compositional and structural inhomogeneities. Since about 24 years we have developed the technology of high pressure sputtering for oxide materials. The technique of sputtering at high oxygen pressures (1 - 4 mbar) allows a smart and homogeneous on-axis in-situ deposition of high-quality metal-oxide thin films from stoichiometric targets avoiding resputtering due to negatively charged oxygen ions. If conventional sputtering pressures of about 0.01 mbar are used for the on-axis deposition of cuprate superconductors, the negatively charged oxygen ions are accelerated towards the heated substrate by the bias potential and they thus resputter copper atoms from the deposited film leaving copper-deficient non-stoichiometric cuprate films. With the high oxygen pressure sputtering technique, this problem is solved by multiple scattering of the oxygen ions at background gas pressures above 1 mbar with subsequent reduction of their kinetic energy down to thermal energies before they reach the substrate. This results in negligible backsputtering of the copper from the deposited films and, consequently, their good stoichiometry and electron transport properties.

High oxygen pressure deposition

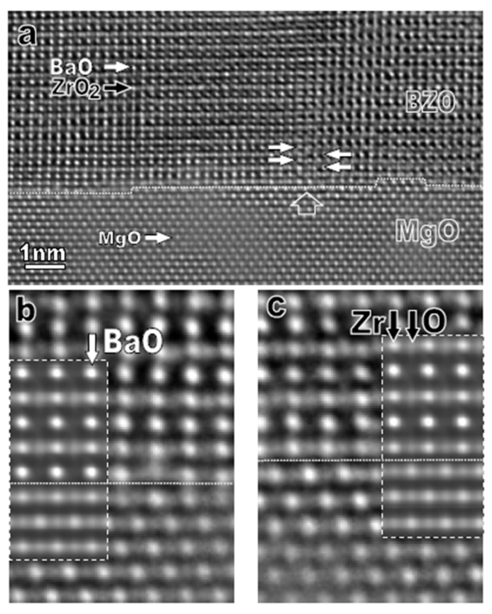
High oxygen pressure sputtering machine.

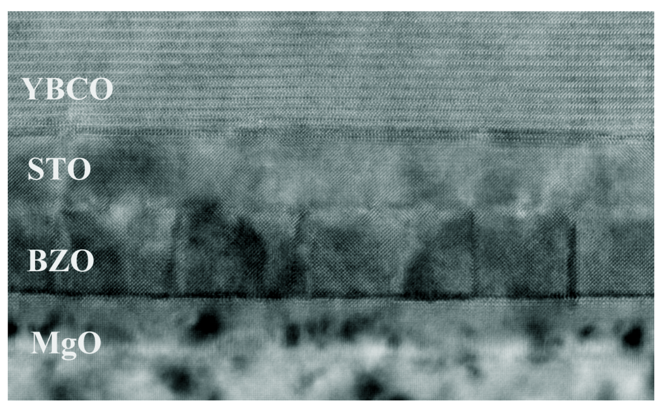


High oxygen pressure magnetron sputtering: photograph of plasma and target holder with YBCO target and a MACOR insulator.



Transfer rod with three sputter heads.

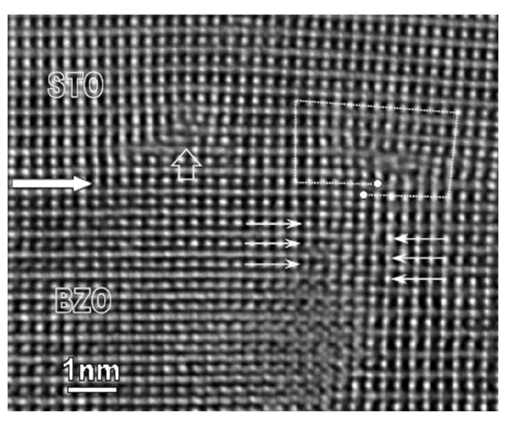




Cross sectional HRTEM image of BZO-STO-YBCO heterostructure deposited on a MgO (100) substrate.

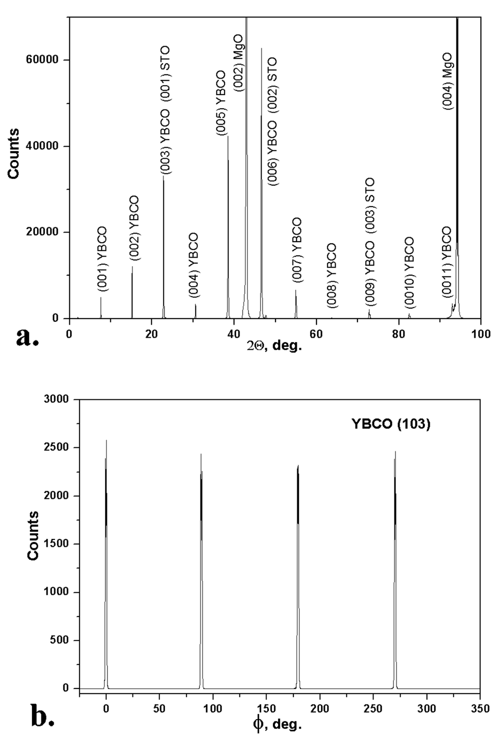
[1$\bar{1}$0] image of BZO/MgO interface area of. The structure change of interface occurs across the interface steps with height of half unit cell. A vertical arrow shows an APB starting at the interface site where the interface structure changes. (b) Magnified image of the interface with a structure of BaO/MgO. (c) Magnified image of the interface with a structure of ZrO2/MgO. The inserts in (b) and (c) show the corresponding calculated images for the specimen thickness of 4.0 nm and a defocus of +8.8 nm.

(S.B.Mi, IFF-8)

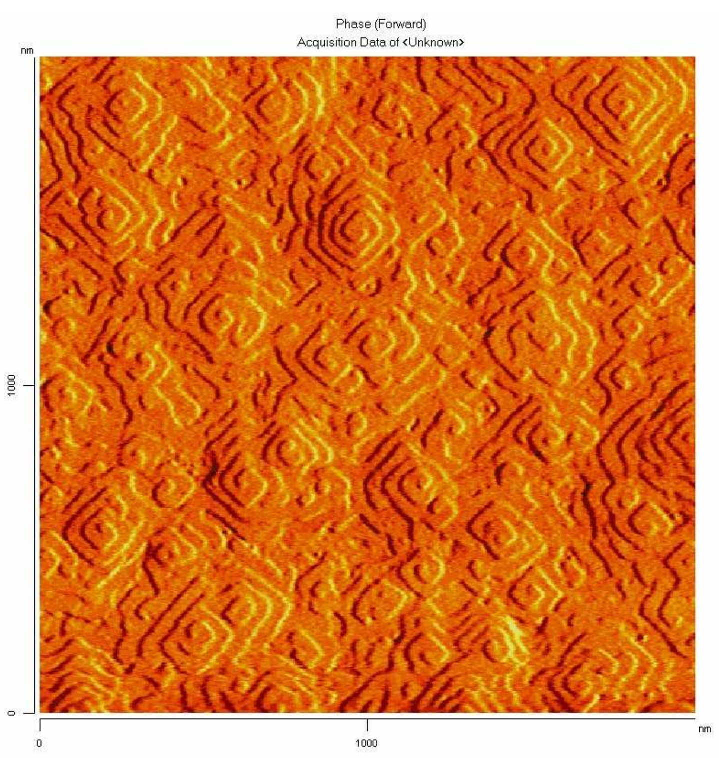


Interface areas of STO/BZO viewed along the [1$\bar{1}$0] zone axis. The horizontal arrows mark the interfaces. The a<100> type misfit dislocations at the interface of STO/BZO are indicated by vertical arrows. A Burgers circuit surrounds a partial dislocation which ends an APB coming from the BZO layer.

(S.B.Mi, IFF-8)



X-ray diffraction (a) Θ-2Θ scan and (b) ϕ scan for YBCO film deposited on a buffered MgO (100) substrate.



AFM image of surface of a 130 nm thick YBCO film: $T_c \approx 93$ K and $I_c \approx 6$ MA/cm² at 77 K.

High quality thin films of the following materials have been produced:

High-T_c superconductors
$YBa_2Cu_3O_7$ · Re $Ba_2Cu_3O_7$ (Re=Pr, Nd, Gd, Ho, Eu) · $Bi_2Sr_2CaCu_2O_y$
$Bi_2Sr_2Ca_2Cu_3O_y$ · (Ba,K)BiO_3 · $Nd_{2-x}(Ce,Sr)_xCuO_4$ · (Tl,Pb)$CaCu_2O_y$

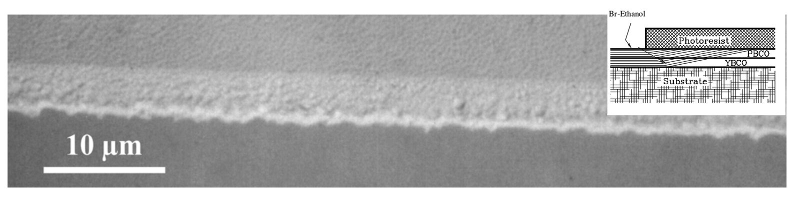
Dielectrics
$SrTiO_3$ · $BaTbO_3$ · CeO_2 · $NdCaAlO_4$ · MgO · Y_2O_3 · YSZ · $LaAlO_3$ · ZnO

Ferroelectrics
$BaTiO_3$ · PZT · $La_2Ti_2O_7$

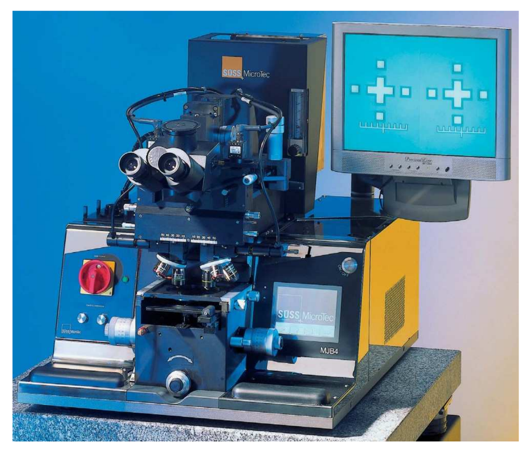
Magnetic Oxides, CMR-materials, etc.
(La,Ca)MnO_3 · (Pr,Sr)MnO_3 · $SrRuO_3$ · $SrCoO_3$

Patterning methods for oxide heterostructures

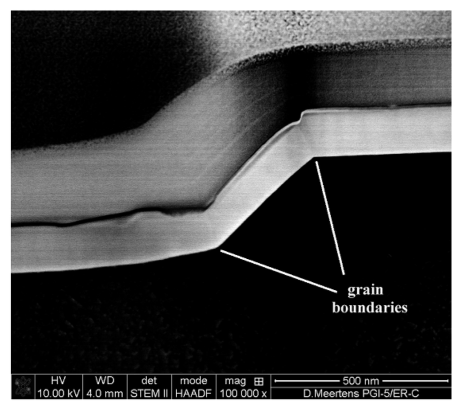
- Used photoresists: PMMA and AZ TX1311 55cP.
- Exposure by a deep-UV (250 nm) mask aligner.
- Patterning of films by a non-aqueous chemical etching in Br-Ethanol, by ion beam etching, by FIB, or by structuring of substrates (step edge junctions).
- Cleaning and heat treatment in oxygen plasma of the oxide heterostructures before deposition of top layers.



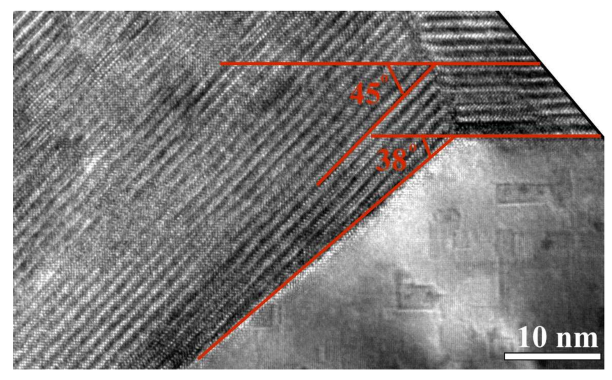
Optical image of a 500-nm thick YBCO-PBCO bilayer etched through a mask of PMMA photoresist by the Br-ethanol solution.



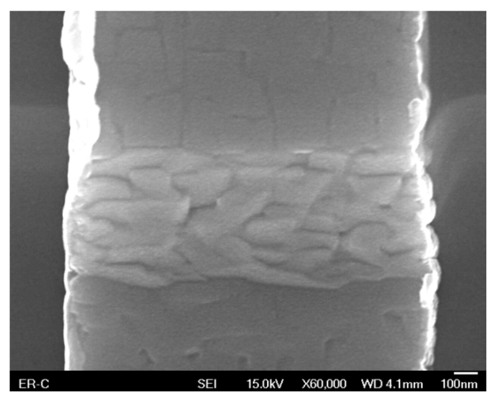
Mask Aligner MJB4 from SÜSS MicroTec with UV250 lamp and optics used for exposure of PMMA and deep-UV AZ photoresists.



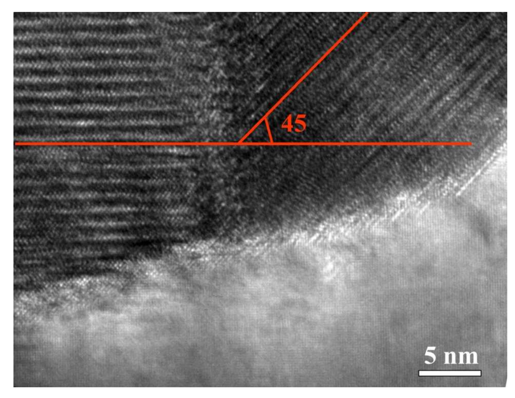
A cross-section of a edge structure made by FIB.



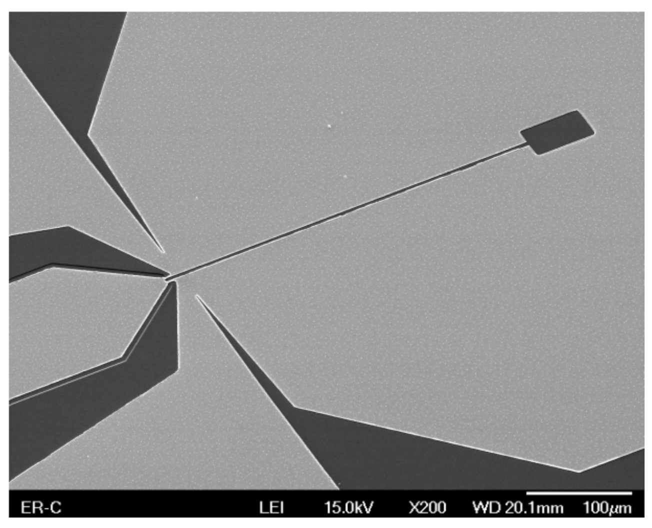
HRTEM image of the YBCO film deposited on the top of the MgO substrate step edge.



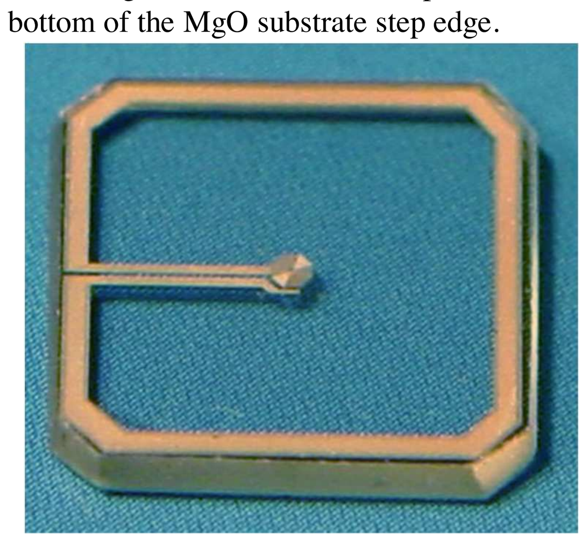
SEM image of a step-edge Josephson junctions.



HRTEM image of the YBCO film deposited on the bottom of the MgO substrate step edge.



SEM image of a high-T_c DC SQUID structure with step edge Josephson junctions used in the high-T_c DC SQUID magnetometers.

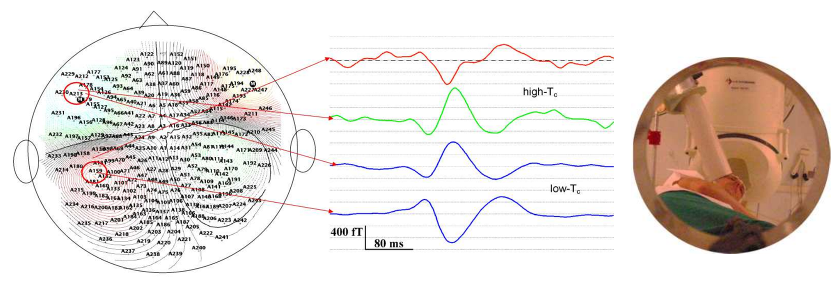


Superconducting multilayer flux transformer used in the high-T_c DC SQUID magnetometers and based on $YBa_2Cu_3O_{7-x}$-$PrBa_2Cu_3O_{7-x}$ -$SrTiO_3$- $YBa_2Cu_3O_{7-x}$ metal oxide heterostructure on MgO substrate with epitaxial $BaZrO_3$-$SrTiO_3$ buffer layer.

Examples of applications

We have used the oxide heterostructures prepared by the high oxygen pressure deposition and different patterning methods mainly for production of high-T_c superconducting devices, for example, SQUIDs (superconducting quantum interference devices), which are integrated in magnetic field measurement systems for magnetic microscopy of microstructures and electric circuits; for geomagnetic surveys; for and biomagnetic measurements; for non-destructive evaluation of materials and many other applications.

Photograph of geomagnetic airborne TEM surveying measurement with 8-channel high-T_c SQUID tensor magnetometer system.



Results of measurements of an auditory evoked field obtained using a high-T_c SQUID sensor (red and green curves) and low-T_c SQUID sensors (blue curves). Right – a photograph of MEG measurement with high-T_c SQUID.

Summary

The use of the high oxygen pressure deposition technique has allowed to produce high quality metal oxide films of high-T_c superconductors, dielectrics, ferroelectrics, magnetic oxides, CMR-materials, etc. Typical superconducting transition temperature of the $YBa_2Cu_3O_{7-x}$ films obtained by this method is about 93 K and their critical current density is about 6 MA/cm² at 77.4 K. For patterning of the metal oxide films and heterostructures a combination of the non-aqueous chemical etching in Br-ethanol solution and ion beam etching was used. Epitaxial growth and patterning of the films were controlled by SEM, AFM, and HRTEM.

[1] U. Poppe et al. (1990) Patent US4965248.

[2] U. Poppe et al., J. Appl. Phys., vol. 71, 5572 (1992).

[3] M. I. Faley, In "*Applications of High-T_c Superconductivity*", ISBN 978-953-307-308-8, 147 (2011).

[4] M. I. Faley and U. Poppe (2010) Patent WO2012051980.

[5] M. I. Faley et al., *Physics Procedia* **36**, 66 (2012). http://dx.doi.org/10.1016/j.phpro.2012.06.131