SURFACE CONDUCTIVITY PROPERTIES OF HIGH-T_C SUPERCONDUCTORS

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1. Introduction

High temperature superconductivity (HTS) was discovered in certain compounds of copper and oxide (cuprates) in 1986 by Bednorz and Müller [1]. The best known high- T_c cuprates are YBa₂Cu₃O_{6+x} (YBCO) and Bi_mSr₂Ca_{n-1}Cu_nO_{2n+m+2} (BSCCO). A lot of work has been done in the field of HTS to understand conductivity properties in both normal and superconducting state due to their complex nature and many potential applications. The undoped parent compounds are Mott insulators and the conductivity properties of these compounds and the critical temperature T_c are strongly affected by the oxygen content [2]. For YBCO, by varying the parameter x between 0 and 1 the conductivity properties continuously change from insulating through semiconducting to metallic (above T_c). Due to relatively low activation energy for the oxygen diffusion, degraded insulating layer with lack of oxygen is spontaneously created on the YBCO surfaces and interfaces [3]. This layer is a serious problem if defined and sharp interface is required. Degradation processes in terms of YBCO/metal junction resistance increase has been studied by several methods [3], but study of degradation on air was not possible by these techniques. Moreover, these methods provide only averaged information over relatively large area.

Until the discovery of superconductivity at temperature of 26 K in iron-based compound $La[O_{1-x}F_x]FeAs$ in 2008 [4], only cuprates have been considered as HTS. Subsequently, lot of iron-based superconducting compounds have been found. They can be divided into four groups according to the mother compound which is later doped. For most compounds, doping is necessary to obtain superconducting properties and significantly influence the conducting properties. Superconductors prepared by doping of LaFeAsO are referred to as "1111" type. Lanthanum can be substituted with another element, e.g. samarium and neodymium. "122" type arise from the doping of BaFe₂As₂, "111" type is based on LiFeAs and "11" type on FeSe. Later two mentioned types have superconducting properties even without doping. Currently, the highest critical temperature of 55 K have been measured in Sm[O_{1-x}F_x]FeAs [5]. Similarly as in cuprates, properties in both normal and superconductive state are significantly dependent on the doping and degradation of surface layer is also an issue.

Cuprates and iron-based superconductors exhibit several similar properties. On the other hand, there are also many important differences. In this work, surface conductivity properties of YBCO and Co-doped BaFe₂As₂ thin films have been investigated by scanning probe microscopy (SPM) methods. YBCO is copper-oxide superconductor with critical

temperature above the boiling point of nitrogen. For parameter x = 0.93, the highest critical temperature of 95 K is achieved [6]. Bellow the Néel temperature and for small values of x, YBCO is an antiferromagnetic insulator [2]. BaFe_{2-x}Co_xAs₂ (Ba-122) belongs to the "122" type of iron-based superconductors. For parameter x = 0.2, its critical temperature is about 22 K.

2. Experimental

High quality *c*-axis oriented YBCO thin films have been prepared by dc magnetron sputtering from a stoichiometric ceramic target on single crystalline LaAlO₃ substrates. Ba-122 thin films have been fabricated by pulsed laser deposition (PLD) on MgO single crystalline substrates with Fe buffer layer. Detail information on the preparation process of the films can be found in [7] and [8].

For all topography and surface conductivity measurements, scanning probe microscopes NT-MDT Solver P-47 Pro and NT-MDT NTEGRA Aura have been used. Topography of thin film has been measured in semicontact atomic force microscopy (AFM) mode with standard silicon AFM tips. For SSRM measurements, which provide simultaneous topography in contact mode and map of local surface conductivity, silicon AFM tips with conductive PtIr-coating have been used. A bias voltage has been applied between the sample and the tip and the resulting current through tip-sample contact has been measured. For Scanning Spreading Resistance Microscopy (SSRM) studies, the sample was biased and the tip was grounded. Measurements had been carried out in air and nitrogen atmosphere at ambient pressure.

For Auger Electron Spectroscopy (AES) measurements, Omicron MULTIPROBE UHV system with SPHERA electron spectrometer has been used. Sample have been etched in ion gun Platar Klan 53M.

3. Results and discussion

Surface topography of HTS thin films is on Fig. 1a and Fig 2a. *C*-axis oriented YBCO thin film prepared by dc magnetron sputtering is relatively rough with rectangular objects and clearly visible grains of irregular shape. On the surface of Ba-122 thin film are rectangular object and there are also low visible cracks in the material.

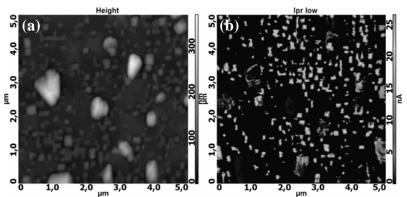


Fig.1: Typical (a) AFM topography measured in semicontact mode and (b) corresponding SSRM image (bias voltage 1.5 V) of YBCO thin films.

From the all SSRM measurements, highly inhomogeneous local conductivity is clearly visible. Bright areas indicate regions with high conductivity. On sputtered YBCO films, there are visible areas with relatively high conductivity through which almost whole current flows. On the other hand, there are also regions with no or immeasurable conductivity. Existence of such areas can be explained by different thickness of the insulating degraded layer on the

YBCO surface. Such variations are probably due to poly-crystalline nature of the film with near-optimally doped grains under the degraded layer. Inhomogeneous oxygen distribution and surface degradation can be caused by enhanced diffusion of the oxygen through grain boundaries and other defects. The thickness of the degraded insulating layer can gradually change from zero through very thin where the transport properties are given by a tunnelling current, up to thick completely insulating layer. Poly-crystallinity of our films was confirmed by SEM. Surface contamination which could cause the variation of oxygen on the surface has been excluded by the AES measurements (Fig. 3).

On Ba-122 thin films, conductivity is less but still inhomogeneous with lower conductivity on the grain boundaries. Spiral pyramidal structures which were created during growth process are clearly visible. Similar structures have been observed on epitaxial YBCO films [9].

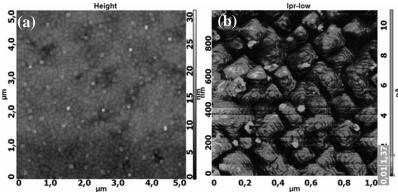


Fig.2: Typical (a) AFM image measured in semicontact mode and (b) SSRM image of smaller area (bias voltage 2.0 V) of Ba-122 thin films.

Such highly inhomogeneous surface conductivity can significantly influence measurements of I-V characteristics, measurement by tunnelling spectroscopy and properties of Josephson junctions prepared by planar technology.

For the degradation studies, sputtered YBCO thin films have been used. Degraded layer have been removed by ion beam etching before the SSRM measurements. Area of $5x5 \mu m$ was repeatedly scanned by the SSRM during several hours. Map of conductivity has been recorded for each scan and consequently average conductivity has been calculated. Linear decrease of average conductivity in time over first 8 h after etching in both air and pure nitrogen atmosphere due to out-diffusion of oxygen has been observed (Fig.4). The degradation process is slightly faster in air due to water vapor which cause further degradation reactions of the YBCO surface.

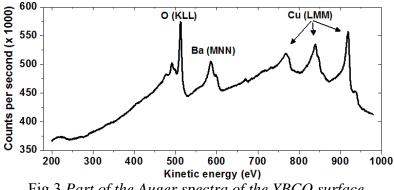


Fig.3 Part of the Auger spectra of the YBCO surface.

4. Conclusions

To conclude, surface conductivity properties of high- T_c superconductors have been investigated by SPM methods. Spiral pyramidal objects created during growth process have been revealed by SSRM on Ba-122 films deposited by PLD. It has been shown that surface conductivity is highly inhomogeneous and should be taken into account when micro-scale planar junctions are measured. Moreover, it can be limiting factor for nano-scale applications. We propose that such inhomogeneous surface conductivity is due to degraded insulating surface layer of varying thickness and inhomogeneous distribution of oxygen near the surface. Gradual decrease of YBCO average surface conductivity in both air and pure nitrogen atmosphere due to out-diffusion of oxygen has been observed by SSRM.

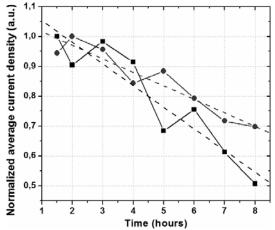


Fig.4: Average SSRM current normalized to maximum value measured on sputtered YBCO thin films in air (squares) and pure nitrogen atmosphere (circles) after the ion beam etching as a function of time.

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