MICROSTRUCTURAL CHANGE OF YSZ– SUPPORTED YBaCuO SUPPERCONDUCTING FILM BY PROTON BEAM BOMBARDMENTS*

Wang Guanghou (王广厚), Luo Chenglin (罗成林), Pan Guoqiang (潘国强), Yan Shiqian (颜石乾), Han Min (韩 民), Yang Senzu (杨森祖), Li Yuan (李 元), Ji Zhengming (吉争鸣), Sun Zhijian (孙志坚) and Wu Peiheng (吴培亨)

(Nanjing University, Nanjing 210008, China)

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ABSTRACT

Microstructural change of YBaCuO film/YSZ substrate with and without proton irradiation has been studied by scanning electron microscope and X– ray diffraction techniques. Structural analysis has shown that conversion from tetragonal to orthorhombic phases, reduction of nonsuperconducting phase and preferential rearrangement of crystal grains are all favorable to the improvement of superconductivity in the YBaCuO film supported by YSZ substrate by proton beam bombardment.

Key words: YBaCuO superconducting film Proton irradiation Scanning electron microscope X – Ray diffraction Conversion of phases

I . INTRODUCTION

The discovery of high temperature oxide superconductors[1,2] has emerged a great attention. More recent experimental and theoretical work have demonstrated that the structural changes can strongly affect the superconductivity and the structure of the superconducting YBaCuO is an orthorhombic phases[3] ($x<0.5$) and has a layered anisotropy. The basic units of this structure consists of the square planar configuration of Cu(1)– O layers forming a two dimensional network and ordered Cu(2)– O layers forming a one dimensional linear chain along the *b* axis. The two Cu(1)– O layers per unit cell are separated by Y atoms. The Ba atoms are situated between the Cu(1)– O and Cu(2)– O layer.

The substitution of Y with other chemically similar elements, including magnetic rare earths does not change the superconductivity, indicating that the interaction between the layers is weak. The transport properties associated with critical current are approximately isotropic in the basal plane, but are very much smaller for current perpendicular to the layers[4]. Therefore, the square Cu(1)– O planes appear to play a vital role in the high *Tc* superconductor. However, the tetragonal phase of

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$YBa_2Cu_3O_{7-x}$ is not superconducting above 4.2K[5]. Major differences between the orthorhombic and the tetragonal structure are due to the vacancies (unoccupied lattice sites) and disordering of O along the one– dimensional chains[3,5]. In general, this ceramic oxide crystallizes in both orthorhombic and tetragonal structures coexist in the sample due to slight differences in its sintering process.

Ion bombardment is one of the efficient means of patterning superconducting oxide films through radiation damage. Laibowitz et al.[6], have patterned $YBa_2Cu_3O_x$ thin film to fabricate and operate at 68K a weak link dc SQUID by oxygen or arsenic ion implantation. We have used the electron and proton beams to irradiate YBaCuO superconducting materials and found different effects on its properties[7], particularly, we have observed a great enhancement of the transition temperature in hydrogen– implanted YBaCuO films supported by YSZ substrate[8]. In this paper we shall have an insight into microstructural alternation of the above films by energetic proton bombardment, and present possible reasons of modification of its superconductivity.

II. EXPERIMENTS AND SUPERCONDUCTING TRANSITION TEMPERATURES

rf magnetically controlled– sputtering– method was used to prepare superconducting films from the $YBa_2Cu_3O_{7-x}$ bulk material. They were deposited onto the yttrium– stabilized– zirconium oxide crystal substrates (YSZ), which were held at 200°C during the deposition.

IM– 200M ion implantor (made in Japan) was used to irradiate the superconducting film with 150 keV protons of a fluence 1.6×10^{16} H/cm^2 under vacuum ($\sim133.33\times10^{-5}$ Pa working pressure).

The electric resistivity of the specimen was measured before and after implantation, by the standard four probe method with temperature change from below liquid nitrogen temperature (62K) to room temperature. Microstructural studies of the superconducting films before and after proton bombardment were analyzed by X– ray diffraction by using CuK monochromatic radiation with a wavelength of 0.15418 nm and a scanning speed of 0.5° and a counting rate of 500 cps, and by scanning electron microscope (SEM, type NIGPA), working at 20 kV, with multiplications of 5400 and 10000, respectively. Both proton implantation and the structural analysis were carried out at 295K (room temperature) and the temperature variations during the measurements were less than ±1.0K.

Table 1 lists the transition temperatures (zero resistance) of several YBaCuO films supported with YSZ substrates before and after proton bombardment. All T_{co} of these samples increase after implantation. It seems that the worst sample with the lowest before proton irradiation has gained the greatest improvement.

Table 1

Change of the transition temperature of YBaCuO superconducting film supported by YSZ substrate

Specimen No.	Substrate	Virgin	Irradiated
370	single cryst. YSZ	63.9K	73.2K
371	single cryst. YSZ	60K 55K*	78K
372	single cryst. YSZ	< 60K 50K*	80K

* These values are the extrapolated due to the limitation of temperature measurements

Ⅲ. X– RAY DIFFRACTION STUDIES

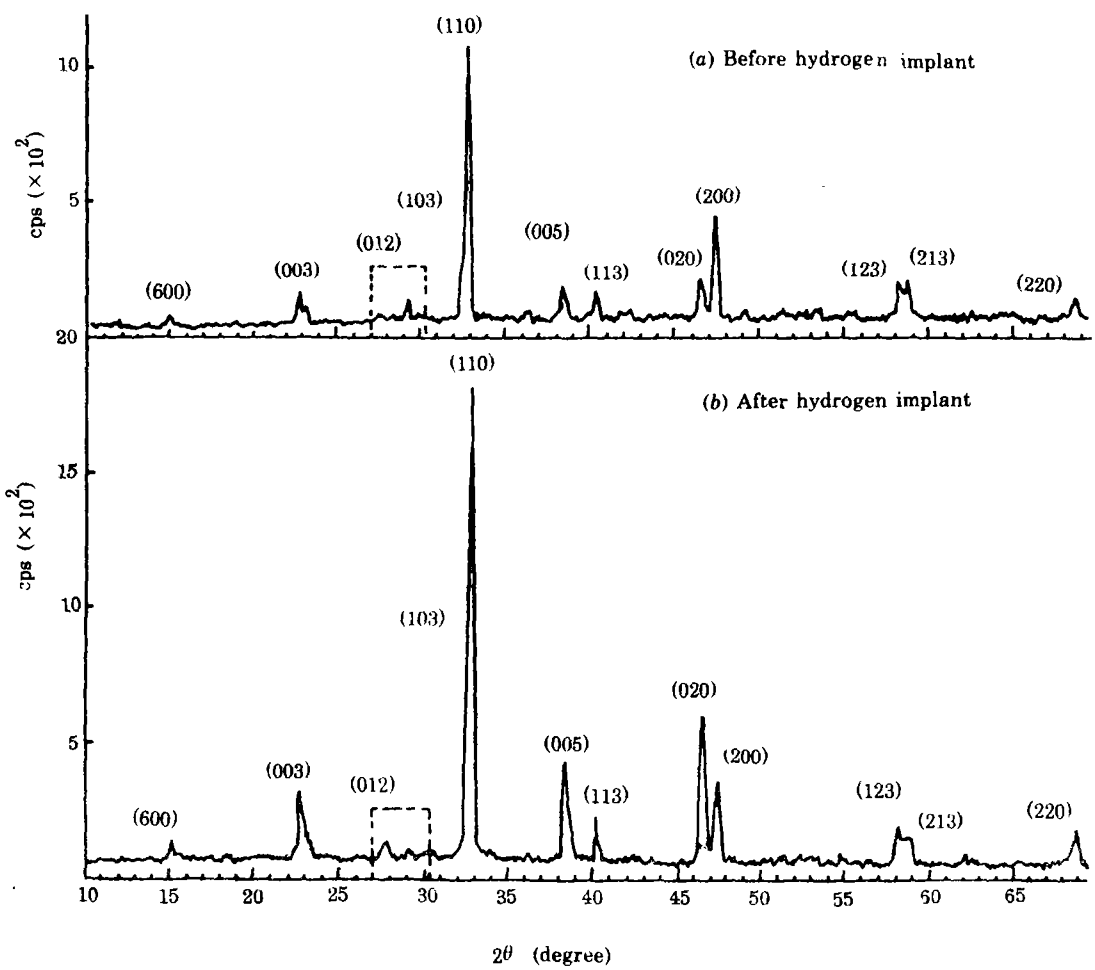

Fig.1 X– ray diffra[illegible]a of YBaCuO superconducting film with YSZ subst[illegible]e and after proton irradiation

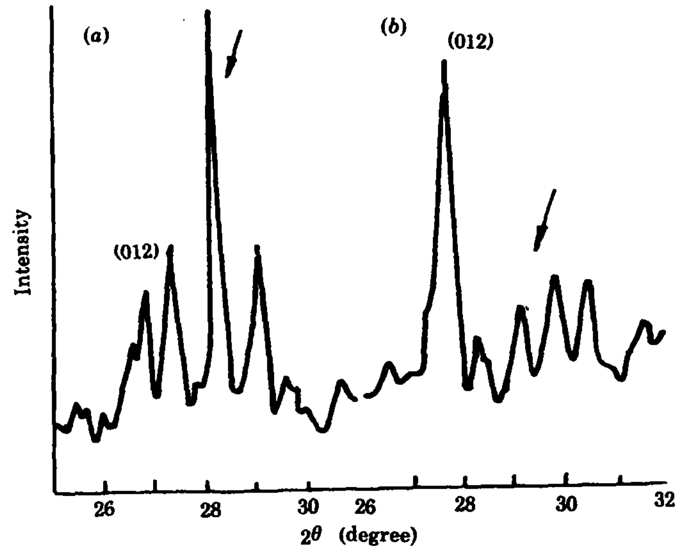

Fig.2 Enlarged diffraction spectra at angles between 26° and 32°, illustrated by the broken line area in Fig.1

Proton irradiation not only modifies the superconductivity of YBaCuO film, but also changes its microstructures[8], which have been studied in detail by X- ray diffraction and scanning electron microscope. Fig.1 presents X- ray diffraction spectra of YBaCuO superconducting film with YSZ substrate before and after hydrogen implantation. Either absolute intensities or relative intensities of X- ray diffractio peaks change dramatically before and after hydrogen implantation, especially for the diffraction planes (012), (005), (113), (020), (200), (123), and (213) etc.. By making a careful investigation of X- ray diffraction, following features are observed from Fig.1 and 2.

1. Conversion from the tetragonal to orthorhombic phases

Although the crystal structures of the tetragonal and orthorhombic phases in YBaCuO system are very similar to each other some pairs of X- ray diffraction peaks can be distinguished, for instance, the diffraction peak from the plane (100) is overlapped with the peak from (003) but separated from the (010) peak in the orthorhombic phase where $b \neq a = c/3$, while the peak from (100) plane is overlapped with the plane (010) and separated from the (003) peak in the tetragonal phase with $b = a \neq c/3$. Therefore, the ratio of intensities I[(003)+(100)] and I(010) in orthorhombic phase is greater than that of intensities I(003) and I[(010)+(100)] in the tetragonal phase. So the same are in the case of planes (006) and (020), (116) and (213) etc.

Table 2 lists the intensity ratios from several diffraction planes described above before and after proton implantation. From which we can see that all ratios are increased after irradiatiom, indicating that the tetragonal- to- orthorhombic phase conversion occurs during proton implantation.

Table 2
The intensity ratios from several diffraction planes before and after proton irradiation

Intensity ratio	Pre- irradiation	Post- irradiation
I[(006)+(200)]/I(020)	0.315	1.63
I[(116)+(213)]/I(123)	0.896	1.43
I[(003)+(100)]/I(010)	1.360	1.543

2. Decrease of nonsuperconducting phase

In virgin sample, some other phases such as Y_2BaCuO_5 (See Fig.2) characterized by the diffraction peak at $2\theta = 29.3^{o}$[10] which is neither orthorhombic nor tetragonal, are greatly reduced by proton irradiation, but the diffraction peaks from (102) plane as well as (110), (005), (200) are greatly enhanced, demonstrating that the superconducting phase is increased with proton bombardment.

3. Shortening of c– axis

For the planes with bigger *c* index the distance *d* is obviously shortened after implantation while *d* does not change much for those with bigger *a* and *b* indexes. The *c* axes of three YBaCuO crystal planes (002), (003), (005) are all shortened after hydrogen implantation, the average value is decreased from 1.1656 nm to 1.1615 nm. The shortening of c– axes implies that Cu– O plane in the orthorhombic phase structure is closer to that in the Cu– O tetrahedron, thus intensifying their interaction and improving its superconductivity.

IV. SCANNING ELECTRON MICROSCOPE OBSERVATION

Fig.3 (*a*,*b*) are the scanning electron micrographs of YBaCuO/YSZ before and after proton irradiation respectively. Fig.3 (*c*) and (*d*) are the corresponding pictures taken with multiplication of 10000 in the case of 20 kV. From these pictures we can see the following characteristics:

(1) Configuration of the crystal grains before hydrogen implantation looks various platelets with different sizes from about 2 to 5 μ m in diameter. In the irradiated sample the crystal grains are bar– typed, and their cross sections are nearly same and have a diameter of ~ 0.2μ m and a length of ~ 1.5μ m. Therefore, hydrogen bombardment makes crystal grains in YBaCuO film finer and more regular.

(2) The crystal grains are much denser in the implanted sample and their density is increased by two orders of magnitude (10^6 cm^{-2} in the virgin sample and 10^8 cm^{-2} in the implanted sample). It looks that the superconducting films become very uniform after proton bombardment.

(3) These bar– type grains in the implanted film have a preferential orientation perpendicular to the substrate surface and are parallel to each other except a few of the bar– typed crystallites lying on the substrate surface with the length nearly equal to the thickness of the YBaCuO superconducting film (~1.5μ m) (See Fig.3 d). It seems that the proton– irradiation promotes recrystallization of YBaCuO superconducting film along certain crystal orientation on the YSZ substrate surface which are more favorable to superconductivity.

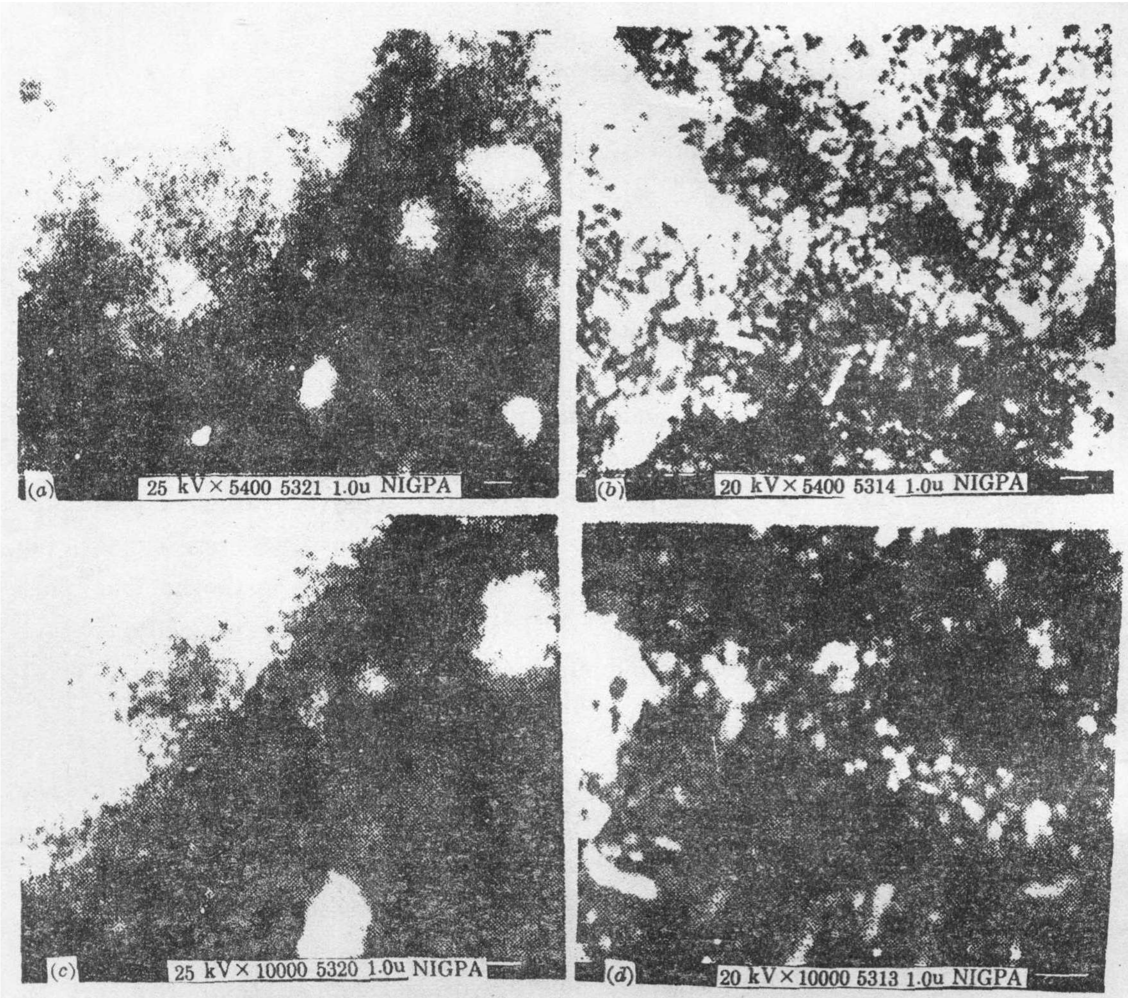

Fig. 3 Scanning electron micrographs of YBaCuO film/YSZ substrate

(*a*) Virgin sample and (*b*) the implanted sample with ×5400 multiplication, (c) and (*d*) are their corresponding pictures with ×10000 multiplication

V. CONCLUSIONS AND DISCUSSIONS

From the above studies we can obtain the following conclusions:

(1) the proton beam irradiation can greatly enhance the transition temperature of YBaCuO films, especially when the range of the energetic protons are close to the thickness of the superconducting films.

(2) Several microstructural changes of the YBaCuO film/YSZ have taken place during the proton bombardment, such as conversion from tetragonal to orthorhombic phases, reduction of impurity phase Y_2BaCuO_5 and shortening of *c*− axis, etc..

(3) The increased density and preferential rearrangement of crystallites in the films

by proton bombardment are also beneficial to the improvement of superconductivity.

Ion implantation as a nonequilibrium process has been used to increase solubility levels above thermal equilibrium values and to produce metastable alloys and to fill vacancies in sublattices of compounds which can not be correctly be formed by conventional techniques. These processes may alter composition, structure and electronic properties of the superconducting film because they can not only dope impurity (hydrogen in this case), but also produce radiation damage in solid, which probably behave as a source of internal pressure, in the same way as in SmS, where they induce an insulator– metal transition[11]. Furthermore, the energy deposition by the protons allows the twin boundaries to move into a more orderly configuration in response to the lattice strains present, thus promoting the preferential rearrangement of crystal grains in YBaCuO film along certain direction of the substrate surface. From high temperature X– ray studies on the phase transition of $YBa_2Cu_3O_7$ material the tetragonal– to– orthorhombic transition begins at around 905K and is completed at 873K when the temperature is lowered [10]. Our proton irradiation has similar function on YBaCuO film.

However, in our previous study of infrared absorption spectroscopy we noticed that Cu– H bonds were formed in the hydrogen– implanted sample[9], which was also beneficial to the superconductivity[12]. At present it is difficult to identify which one has a predominant role in improving superconductivity of YBaCuO film/YSZ by the proton irradiation. Further detail studies of proton– implanted ceramic oxide superconductor with different energies and doses are being performed by various methods in order to have a better understanding of mechanism of proton beam modification of the superconducting film and make it useful in preparing high quality of the samples.

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