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In-situ Characterization of Electronic Structure of Engineered Surfaces of c-axis YBCO films for Sandwich type Junctions

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Crystallinity electronic structure of engineered surfaces of c-YBCO films for engineered interface barrier of sandwich type Josephson junctions, have been investigated. In order to clarify their re-crystallization mechanism in the subsequent process, especially, change of their depth-profile as a function of subsequent annealing conditions has been characterized by angle resolve X-ray / ultraviolet photoemission spectroscopy (XPS/UPS). The engineered surfaces fabricated by irradiation of an ECR-Ar ion beam exhibited an amorphous structure with an insulator like electronic structure. A gradual narrowing of this gap was observed, though of internal region of this annealed surface started to be converted to the 123 structure. This re-crystallization phenomenon depended on both post-annealing and the irradiation conditions. For the amorphous layer created by the irradiation of Ar ion with a kinetic energy of 500 eV, the annealing at 630 ℃ for 1 h is sufficient to convert it into the metallic 123 structure. For the surfaces treated by the 1 keV Ar ion beam, the insulating feature was conserved even surface after the identical annealing. After the annealing of 630 ℃-4 hour, there-crystallization took place over the 1 keV irradiated surfaces. Photoelectron take-off angle dependence of these annealed surfaces revealed that the re-crystallization should start at the initial amorphous / YBCO interface and propagate toward the top layer. A combination of the higher energy irradiation and shorter time of subsequent processes are desirable for conserving the non-superconducting properties of the engineered interface.
Key words: HTS, Josephson Junction, Sandwich, EIB, Electronic Structure

1. INTRODUCTION

For Josephson junctions of all-high temperature superconductors, an adoption of so-called engineered interface barrier has resulted in a significant improvement in junction performances and suppression of spreads of junction characteristics, which recently almost satisfy the requirements for small-scale integration [1-13]. The most remarkable improvement in the reduction of spreads of critical current density and normal-state resistance below several percents has been achieved in ramp-edge type of junctions [4-13]. Adoption of so-called engineered interface barrier, instead of insertion of artificial layer between the superconducting electrodes, is a key for the significant improvement.

Though the performance and reproducibility of conventional sandwich type of junction, of which superconducting electrodes are c-axis oriented HTS epitaxial layers, are still not equivalent to the ramp-edge ones, it principally has advantages for higher-level integration, such as well-definable junction-area and degree of freedom in device-arrangement. According to the potential of the sandwich type of junctions, the engineering-interface process is recently adopted in their barrier-layer fabrication. Noteworthy improvements in transport properties and their spreads of the c-axis stacking junctions start to appear. [1-3]. Superconducting-short or flux-low type of properties are, however, often reported. For establishing fabrication-process of the sandwich junctions, it is desired to directly clarify microscopic nature of the engineered layers over HTS electrode with the c-axis preferred orientation, and its stability during counter-electrode formation processes.

In this study, we have carried out *in-situ* characterization of engineered surfaces over c-axis YBCO epitaxial films by means of photoemission spectroscopy and reflection high-energy electron diffraction (RHEED). A relationship between surface-nature, including chemical formula, crystal- and electronic-structure, stability during subsequent high temperature-process and engineering-conditions are clarified.

2. EXPERIMENTAL PROCEDURE

YBCO films 2000 Å thick grown on (001) plane on MgO or $SrTiO_3$ by 90 degree off-axis sputtering were used as specimens. Their epitaxial growth along the c-axis, and the surface roughness were confirmed by streaky RHEED patterns with spacing corresponding to a real-space lattice parameter about 3.85 Å and four-hold azimuthal symmetry. Superconducting

transition temperature $T_{c(\rho=0)}$ of the films was above 89 K. Details of the sample preparation has been reported in our previous paper [14]. An attractive feature of this system is all of the surface-engineering, subsequent annealing which simulates the fabrication process of counter electrode, and surface characterization at each step can be performed *in-situ*.

Initial modification of the surfaces was performed by using Ar ion beam generated by electron cyclotron resonance type ion source under the following conditions; kinetic energy of Ar^+ ions = 500 ~ 1000 eV, etching time = 30 ~ 300 sec, incidence angle of the Ar^+ beam with respect to surface-normal of 41 deg., sample temperature < 50 °C. An etching rate at the ion kinetic energy of 1 keV was about 10 Å/sec. Since the beam was operated under so-called space-charge limited region where integrated energy of the ion irradiation is proportional to the two and a half power of the kinetic energy, the integrated energy on the conditions of 500 eV-180 sec, 750 V-60 sec and 1 keV-30 sec is almost identical. The etching time was varied for investigating an effect of the integrated energy. Before and after the etching, there was no detectable degradation in temperature-resistivity characteristics of the specimens, which means just thin surface layer should be modified by this treatment. After the etching, crystal structure, composition and electronic structure are examined in high vacuum in the range of low 10^{-10} Torr by means of *in-situ* RHEED, X-ray photoemission spectroscopy (XPS) at room temperature. The surface composition was calculated from XPS signals of Cu $2p_{3/2}$, Ba4d and Y 3d core levels. After the first measurement, the surfaces were annealed under an incidence of atomic oxygen beam with flux density above $1x10^{15}$ atoms•cm^2•sec. This oxidizing atmosphere is sufficient to grow high T_c YBCO films by MBE or co-evaporation. Then, the subsequent measurements were preformed.

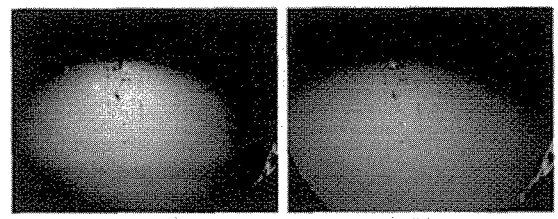
3. RESULTS AND DISCUSSION

For all of the treated surfaces, a halo pattern is observed in RHEED measurement taken under a glazing incidence of the primary electron beam. Broad diffraction spots of the 123 structure were observed in high incidence-angle patterns of the surfaces irradiated with the 500 eV beam. On the other hand, for the surfaces etched with the 1 keV beam, the halo patterns were conserved against any change of the incidence angle. These results means that the amorphous layer of the surface was created by the Ar ion beam irradiation and the thickness of this layer depend on kinetic energy of the Ar ions. The etching also resulted in obvious compositional changes. In the early stage of the etching, the composition moves toward the Y-rich side, which seems reasonable since Y-O has the lowest sputtering yield among the constituent oxides of YBCO. It is noteworthy that the surface composition depends not simply on the kinetic energy of the bombarding ions or etching time but on the integrated irradiation energy proportional to the product of [ion flux]×[ion energy] ×[etching time]. With the total irradiation energy increased, saturation is observed in the ratio of the cations on the surface, though the compositional deviation with respect to the intrinsic surface is slightly enhanced with a rise of the kinetic energy.

A change of the degree of oxidation of the engineered surfaces was characterized by the Cu $2p_{3/2}$ core peak, because the intensity of the so-called satellite peak corresponding to the $\underline{2p}^5 3d^9$ final state in this signal is sensitive to oxygen concentration. Figure 2 shows the change of Cu $2p_{3/2}$ XPS spectra of ion beam etched surfaces of c-YBCO films with kinetic evergy of Ar ions

TABLE I
SURFACE-COMPOSITION OF ENGINEERED C-YBCO FILMS

Ar^+ Beam Energy	Etching Time (sec)	Y	Ba	Cu (at. %)
1 keV	30	39	36	25
500 eV	40	25 ~ 27	32~34	39~43
500 eV	180	40	34	26



(a) (b)

Fig.1 RHEED patterns of the 500 eV-180 sec (a) and 1 keV-40 sec (b) etched surfaces taken under high incidence angle of the primary electron beam.

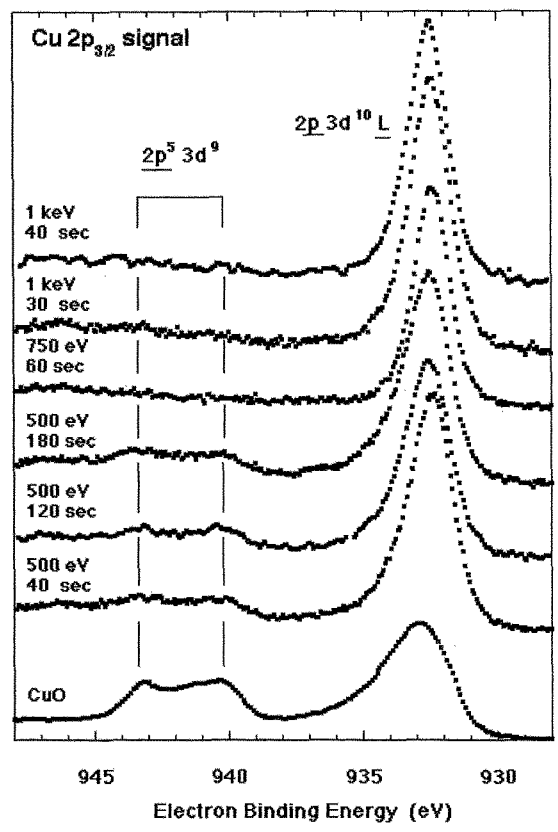


Fig.2 Change of Cu $2p_{3/2}$ XPS spectra of ion beam etched surfaces of c-YBCO films with kinetic Energy of Ar ions and etching time. Spectrum of CuO is shown as a reference

and etching time. In these surfaces, Cu ions were monovalent. On the other hand, the satellite originating in the divalent state remained in the 500 eV-etched surfaces even after an etching with equivalent total irradiation energy. These results mean that the ion beam etching should convert surfaces of the c-YBCO films to Y-rich amorphous ones, where the surface composition should be dominated by the integrated energy of irradiation and the thickness should be increased with a rise of kinetic energy of the bombarding ions.

For examining the thermal stability of the engineered surfaces, changes of crystal and electronic structure were studied as a function of annealing time and temperature T_{ann} up to 750 °C. Figure 3 shows RHEED patterns of the 500 eV-180 sec (a) and 1 keV-40 sec (b) etched surfaces taken after the annealing at 650 °C for 1 hour. For the 1 keV-etched surface, diffraction spots starts to appear at T_{ann} of 630 °C, of which contrast is enhanced in the 720 °C annealed pattern. Symmetry of these patterns is far from that of YBCO and looks like a superposition of patterns of Y_2BaCuO_5 and $BaCuO_2$. On the other hand, in the patters of the 500 eV-etched surface, broad streaks starts to be observable by the 630 °C annealing for 1 hour. The latter pattern has a similar inter-streak spacing and azimuthal symmetry as the underlying c-plane of YBCO film. This re-crystallization process depends on not only T_{ann} but also the annealing time. Even for the surfaces with the high-energy beam, an elongation of the annealing shows RHEED patterns of the 1 keV-30 sec etched surfaces annealed for 4 hours. Even for the intensively etched surfaces, the spotty patterns were converted to the 123 structure-like streaky ones by an elongated annealing time. The 630 °C-4 hour annealing resulted in the almost full conversion.

The observed changes of the engineered surfaces with the annealing indicate the similarity between the conventional equilibrium process and the re-crystallization of the modified surfaces; in the former, the 123 structure grows from liquid phase via a mixture-state of the Y_2BaCuO_5 and liquid [15], whereas in the latter, the as-etched surface with amorphous structure may behave like liquid and the compositional deviation with respect to that of the equilibrium might be relaxed by the nucleation of the $BaCuO_2$. These results reveal a dynamic character of the re-crystallization process where both temperature and time of the annealing are dominating factors.

The recovery to the 123 structure at a rather low temperature around 630 °C, which is well below the usual deposition temperature of YBCO upper electrode, and the similarity of the azimuthal symmetries of the RHEED patterns of the re-crystallized surfaces and the original YBCO films indicate that the conversion of the engineered surfaces to the 123 structure should be dominated by a epitaxial growth. From the standpoints of optimization of the junction processes, it is important to clarify the details of the re-crystallization. In this study, depth profiles of chemical bond nature of the engineered surfaces were, therefore, examined as a function of the annealing conditions.

Figure 4 shows a photoelectron take-off angle $\theta_{take\text{-}off}$ dependence of valence band UPS spectra of the surfaces irradiated with the 500 eV-Ar ion beam for 180 sec and annealed at 600 °C-1 hour. $\theta_{take\text{-}off}$ is defined as the angle between the vector of the incident X-ray and the surface-normal. In the spectrum taken at $\theta_{take\text{-}off}$ of 55 °, the annealing yielded a finite spectral weight at Fermi level. In the spectrum taken at $\theta_{take\text{-}off}$ of 85 °, the insulating feature was conserved even after the annealing, though energy spacing between the valence band maximum and Fermi level was remarkably reduced from about 2 eV of the as-etched surface. These results indicate that the conversion to the metallic 123 phase in the inner region of the engineered surface might be faster than in the outermost regions. These results also mean that amorphous structure of the engineered surfaces by the low kinetic energy ion beam should be rather unstable.

In comparison with the low kinetic energy irradiated surfaces, the insulating feature of the surfaces irradiated with the1 keV-beam was more robust against the high temperature annealing. Figure 5 shows $\theta_{take\text{-}off}$ dependence of Ba 4d signals of the surface irradiated with 1 keV-beam for 40 sec and annealed at 650 °C for 1h. The take-off angle $\theta_{take\text{-}off}$ = 15 and 75 ° corresponded to probing depth about 4.8 and 1.5 nm, respectively. Major part of the signals taken at $\theta_{take\text{-}off}$ = 15

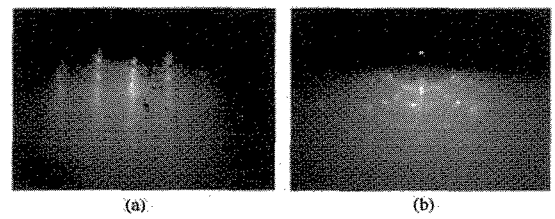


Fig.3 RHEED patterns of the 500 eV-180 sec (a) and 1 keV-40 sec (b) etched surfaces taken after the *in-situ* annealing at 650 °C for 1 hour under the incidence of the O* beam.

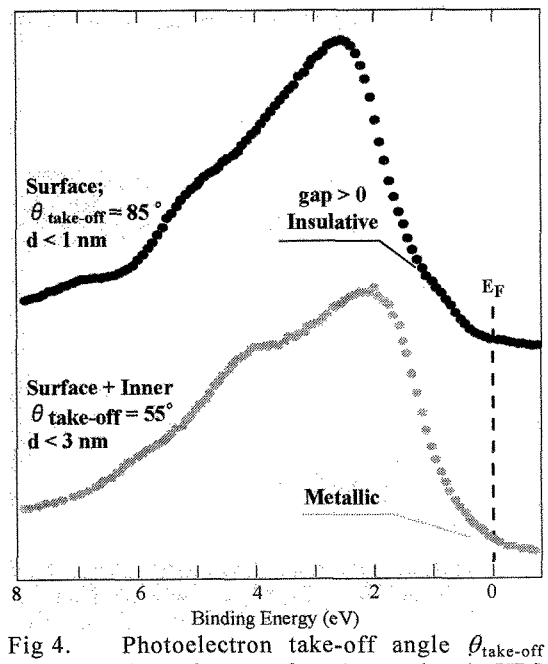


Fig 4. Photoelectron take-off angle $\theta_{take\text{-}off}$ dependence of valence band UPS spectra of c-YBCO etched with 500 eV Ar^+ beam for 180 sec and annealed at 600 °C for 1 h.

Table II Change of photoelectron take-off angle $\theta_{take\text{-}off}$ dependence (depth-profile) of surface composition of the surface modified by the 1 keV – 40 sec etching with the annealing conditions.

	600 ℃ - 45 min			650 ℃ - 1h			650 ℃ - 2h			
$\theta_{take\text{-}off}$ (deg.)	Y	Ba	Cu	Y	Ba	Cu	Y	Ba	Cu	(at.%)
15	29	42	29	32	45	23	19	39	41	
35	29	47	24	34	49	18	20	44	35	
55	29	48	23	33	50	16	18	48	34	
75	21	49	30	26	56	18	14	48	38	

and 75 ° is, therefore, consist of the internal and surface component, respectively. In the spectrum of $\theta_{take\text{-}off}$ = 75 °, the peak located at 89.5 eV, far from the intrinsic signal of YBCO. With a decrease of $\theta_{take\text{-}off}$, the peak gradually shifted towards the lower binding energy side. It means that, in this high-energy irradiated and moderately annealed surface, the inner region should have a structure closer to the YBCO than the outer region. Consequently, these results revealed that the re-crystallization of engineered surfaces started not from the outermost layer but from the internal region. The elongation of the annealing time suppressed the structural variation along the depth-direction. After the 650 °C - 2 h annealing, the photoemission spectra got almost independent of $\theta_{take\text{-}off}$. It is clear evidence that the re-crystallization should be almost completed up to the top. As an exception, the spectrum taken at $\theta_{take\text{-}off}$ = 75 ° was a little bit different from the others. Origin of this is not clear yet. It might be affected by extrinsic effects such as local-oxygen depletion and/or surface contaminations, because of a necessity of long accumulation time of this glazing angle measurement.

The consistent change of the $\theta_{take\text{-}off}$ dependence was observed in valence band spectra of the 1 keV-40 sec etched surface. For the surface annealed at 650 °C for 1 hour, the metallic feature was only observed in a low $\theta_{take\text{-}off}$ region below 15 °. The insulation gap gradually opened with an increase of $\theta_{take\text{-}off}$. On the other hand, after the 650 °C for 2 hour annealing, the spectra got independent of $\theta_{take\text{-}off}$ and a finite electron density of states was observed all over the conditions of $\theta_{take\text{-}off}$.

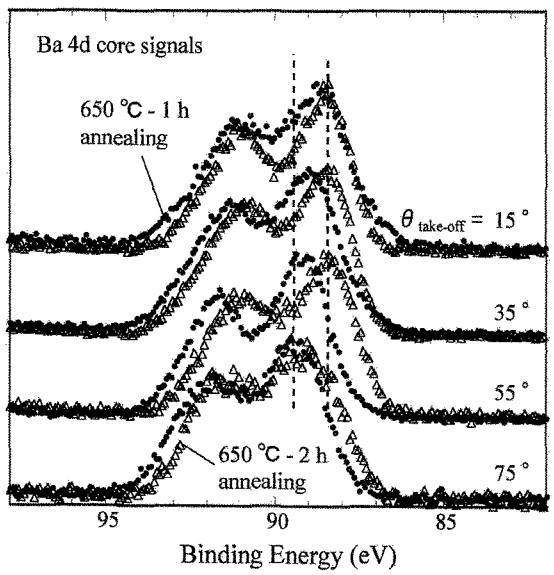


Fig.5 Change of photoelectron take-off angle $\theta_{take\text{-}off}$ dependence of Ba 4d core signals of the 1000 eV-40 sec surface with the duration of the annealing at 650 °C.

Table II shows the $\theta_{take\text{-}off}$ dependence of the surface composition of the surface modified with the 1 keV Ar^+ beam for 40 sec and annealed under various conditions. The higher annealing temperature and the longer annealing time should cause an approach of surface composition towards that of the 123 structure. It should be emphasized that, among the data taken at $\theta_{take\text{-}off}$ below 55 °, the composition gets closer to the 123 structure with a decrease of $\theta_{take\text{-}off}$. This result reveals the presence of the compositional distribution along the depth-direction in the moderately annealed engineered surfaces, where the inner regions should have a composition closer to the 123 structure. A deviation from this tendency observed in the data taken at $\theta_{take\text{-}off}$ =75 ° might be due to the same origins above-mentioned. In UPS spectra, a tendency similar to the take-off angle dependence was observed. For example, the metal-like feature was observed in the He-I spectra of the 600 ℃ - 1 h annealed surface, whereas an insulating structure remained in the spectra obtained by He II excitation with a higher surface sensitivity. Consequently, these results indicate that the re-crystallization of engineered surfaces start at the initial amorphous / YBCO interface and propagate toward the top layer. The phenomenon of that the surfaces treated by high energy irradiation, an insulating feature was conserved after the short time annealing, and the surface treated by the 500 eV-beam irradiation should be converted to a metallic YBCO-123 structure by a rather low temperature and a short time annealing.

In order to clarify the effect of the re-crystallization phenomenon mentioned above, transport properties of c-YBCO/engineered interface barrier/c-YBCO junctions were examined. In this experiment, the YBCO counter electrodes were deposited at 720 °C with various process times. Superconducting current of the specimens with the counter electrodes deposited within 90 min showed a response to magnetic field with degree of modulation above 50 %. A deposition time of the counter electrode longer than 3 hours resulted in a serious suppression of the response. The results of the sandwich junctions also support the re-crystallization mechanism revealed in this study.

4. CONCLUSION

Crystallinity, electronic structure and re-crystallization mechanism of the surfaces of c-YBCO films modified by ion beam irradiation, for engineered

interface barrier of sandwich type Josephson junctions, have been investigated by utilizing a combination of *in-situ* annealing under the oxidizing condition, which has simulated a counter YBCO electrode fabrication process, and *in-situ* ARXPS/UPS. The changes of the valence band spectra and Ba core signals showed that the re-crystallization of the amorphous surfaces, which were created by the irradiation should start at a rather low temperature around 600 °C. The photoelectron take-off angle dependence of the annealed surfaces revealed that the re-crystallization should start at the interface between the amorphous region and the underlying YBCO. The re-crystallization should propagate toward the top layer. This study also revealed that the initial thickness of the amorphous layer should increase as a function of the kinetic energy of the irradiating ions. The combination of the higher energy irradiation and shortening of the counter electrode formation process are desirable for conserving the non-superconducting properties for the engineered interface. The present study reveals that the global optimization of the surface-engineering process and subsequent high temperature process are keys for obtaining a proper tunneling barrier, and that *in-situ* characterization should be important for establishing process fundamentals, and useful for development of various multi-layered devices.

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