High Tc Oxide Superconducting Films for RF Cavities

Kiyomitsu ASANO and Kazuhiro YOSHIHARA*

National Laboratory for High Energy Physics

1-1 Oho, Tsukuba-shi, Ibaraki-ken, 305, Japan

*National Research Institute for Metals

1-2-1 Sengen, Tsukuba-shi, Ibaraki-ken, 305, Japan

In KEK, an R&D on the high Tc superconducting films is underway to investigate possible application to the high gradient accelerating structure. We have prepared the high Tc superconducting YBaCuO (Tc $\simeq$ 90 K) films on Cu and Ag substrates with RF magnetron sputtering and low-pressure plasma spraying methods. We introduced buffer layers to prevent the Cu diffusion into the YBaCuO film from the Cu substrate. When the YBaCuO films on metal substrates were heated at 200°C for 2 hours in ultrahigh vacuum, the surface compositions of the films showed no change into about 10,000 Å in depth, and the films kept Tc $\simeq$ 90 K. Almost no contamination was detected with Auger electron spectroscopy even after air exposure and mechanical polishing. The surfaces of the plasma sprayed films were rougher than those of the magnetron sputtered films. However, the plasma spraying method is very suitable for coating the YBaCuO film onto a metal plate with large surface areas and the inner surface of a cylinder. The quality of the YBaCuO film (Jc = 3000 A/cm^2 at 77 K) was improved greatly by the flux method using a low-pressure plasma spraying. By this method, we are now fabricating the fully high Tc superconducting RF cavity made of the YBaCuO film inside the 3 GHz TE_{011} mode Cu cavity.

1. Introduction

In KEK, an R&D on the high Tc superconducting film is underway to investigate possible application to the high gradient accelerating structure[1)2)].

The high Tc oxide superconductors have several potential advantages over Nb for superconducting RF cavities as follows. (1) For ideal YBaCuO surfaces, one expect to rearch very high accelerating fields of 400 MV/m, compared with 50 MV/m for ideal Nb surfaces. (2) The RF surface resistance of YBaCuO (Tc = 90K) at 77 K is smaller than that of Nb (Tc = 9.2 K) at 4.2 K from the theoretical point of view.

The high Tc oxide superconducting material used for the superconducting RF cavity is required to have the following characteristics. (1) rigid, pure, uniform, dense, smooth, stable, clean, etc., (2) no oxygen desorption even though it is heated in vacuum, (3) high mechanical strength, (4) little effect of grain boundaries on RF superconducting properties, (5) non-magnetic, (6) for the deposited films, sufficient adhesion between substrates and films under thermal cyclic test.

The sintered bulk YBaCuO generally does not satisfy (1), (2), (3), (4) conditions. Therefore, it may be not suitable for the high gradient accelerating structure.

As a candidate for the high Tc superconducting RF cavity, we are testing YBaCuO thin and thick films on various metal substrates. Recent microwave measurements on $Y_1Ba_2Cu_3O_{7-x}$ single crystals and oriented thin films have shown significantly reduced residual losses and improved high-field performance. At 77 K, the RF performance of $Y_1Ba_2Cu_3O_{7-x}$ with c-axis perpendicular to the surface approaches the one of Nb at the equivalent temperature of 7.7 K[3)4)]. Recently Bohn et al.[5)] reported that a bulk polycrystalline YBaCuO remained superconducting in RF fields as high as 640 gauss at 77 K. For T*l*BaCaCuO thin films, the 9.5 GHz surface resistance at 77 K is ten times smaller than that of Cu (9 mΩ) at the same temperature and frequency[6)].

We have prepared the high Tc superconducting YBaCuO films (Tc = 90 K) on Cu and Ag substrates using RF magnetron sputtering and low-pressure plasma spraying

methods. And we adopted the low-pressure plasma spraying method[7] to obtain the uniform YBaCuO film on the inner surface of an RF cavity. We are now fabricating the fully high Tc cavity made of the YBaCuO film inside the 3 GHz TE_{011} mode Cu cavity.

2. Sintered Bulk YBaCuO

Fig. 1 shows the typical SEM photographs for the sintered bulk and thin film of $Y_1Ba_2Cu_3O_{7-x}$. Zero resistance was achieved at 86 K or above, and the 10 – 90 % transition width was less than 2 K. The Meissner effect was also confirmed at 77 K. We prepared the sintered YBaCuO showing Tc $\simeq$ 90 K on 9 May 1987 in KEK. Powders of Y_2O_3, $BaCO_3$ and CuO (4N grade) were mixed and ground at the desired compositions for 1 hour. The mixtures were pre-sintered at 930°C for 24 hours in air and then pulverized for 1 hour. The re-ground mixtures were pressed at an applied pressure of 2 t/cm^2 for 5 min to produce pellets. The pellets were sintered at 930°C for 36 hours in air or an oxygen flow and cooled to room temperature in the furnace. The structure of the samples was examined by X-ray diffraction analysis with monochromated Cu Kα radiation. Resistance measurement was made by the four point method. The conducting silver paste was used to make electrical contact. The surface of the sample was investigated by Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS) and secondary electron microscope (SEM).

The main results are as follows.

(1) The sintered bulk YBaCuO is very porous as shown in **Fig. 1**. We observed that it showed oxygen desorption in vacuum and gradual lowering of Tc.

(2) The repeated measurements of resistance from room temperature to 77 K deteriorated the surface, and consequently Meissner effect disappeared. This is attributed to chemical reaction with moisture.

(3) The weak link of the grain boundary for the sintered bulk YBaCuO leads to low Jc and severe magnetic dependence.

(4) The thermal conductivity of this sintered bulk YBaCuO is very low.

These results show that the bulk oxide superconductors are not suitable for applications to RF cavities for particle accelerators. At this stage, we think it difficult to improve the RF superconducting properties for the bulk sintered ceramics to be competitive with Nb at 4.2 K. The complete ceramic cavity made of the bulk YBaCuO is not applicable to accelerators.

3. YBaCuO films on metal substrates

We have prepared the high Tc superconducting YBaCuO films (Tc $\simeq$ 90 K) on Cu and Ag substrates. At first we tried the RF magnetron sputtering method to obtain YBaCuO films on 13 July 1987 in KEK. We reformed usual RF sputtering apparatus to obtain high Tc films as shown in **Fig. 2** schematically. The sputtering conditions are shown in **Table 1**.

We investigated the sputtered YBaCuO film with XPS, AES, SEM and X-ray diffraction. We found that Cu-rich YBaCuO films was obtained on Cu substrates. The Cu substrate did not produce superconducting films after annealing at about 900°C. This is attributed to the Cu diffusion from the substrate into YBaCuO film during annealing. We introduced buffer layers to prevent the Cu diffusion into the YBaCuO film from Cu substrate. We tested Ag, Ni and Pt platings as the buffer layers.

The quality of the sputtered film was very sensitive to many sputtering parameters. It was very difficult to obtain the uniform $Y_1Ba_2Cu_3O_{7-x}$ film over the large substrate surface. The stoichiometry of the film also depends on the distance between substrate and target. We think that the RF magnetron sputtering method is not suitable for coating the uniform $Y_1Ba_2Cu_3O_{7-x}$ film over the inner surface of an RF cavity.

As a new method for coating high Tc spuerconducting films onto metal substrates, we adopted a low-pressure plasma spraying method[7] in September 1988. We found that this method was very suitable for coating uniform high Tc films over the inner surfaces of RF cavities. The experimental apparatus is shown in **Fig. 3**. A plasma

gun for coating large surface-areas is shown schematically in this figure. Machine mounted plasma spray guns for coating internal surfaces are also available. The low-pressure plasma spraying produces the high Tc films with the high quality of deposits, compared with the conventional plasma spraying in an open air. The quality of the YBaCuO film was improved greatly by the flux method[8] using the low-pressure plasma spraying. The dense superconducting YBaCuO film (Jc = 3000 A/cm^2 at 77 K) was formed on the metal plate after annealing in O_2 atmosphere at about 950°C[8]. The improved method is shown in **Fig. 4** schematically.

As a first step to make a complete high Tc cavity, the YBaCuO film with about 50 μm thickness was coated uniformly on the end plate (150 mmϕ) of TE_{011} mode Cu cavity at 3 GHz. We used a Ag substrate and a Ni-plated Cu substrate as the end plate of the cavity. The YBaCuO thick film was also formed on the inner surface of the cylindrical cavity wall (88 mm length). Using the internal or usual spray guns, we are investigating to coat the YBaCuO film automatically on whole area of inner surface of TM_{010} mode single-cell Cu cavity at 508 MHz.

4. Materials for the substrates and buffer layers

We must use metal substrate to apply high Tc oxide superconducting film to an RF cavity. The characteristics required to the metal substrate are as follows.

(1) high thermal conductivity,

(2) high melting point (≳ 1000°C),

(3) low vapor pressure at annealing temperature (~ 950°C),

(4) non-magnetic material,

(5) thermal expansion is nearly equal to that of the high Tc film,

(6) the high Tc film does not react with the substrate or buffer layers.

The YBaCuO film on the Ag substrate has to be annealed at temperatures between 900°C and 950°C. The film on the Nb substrate exfoliated. This is attsibuted to the difference of thermal expansion coefficients. The Fe diffusion was observed for the 304

stainless steel substrate. The good superconducting properties of films are obtained for the Ni-base alloy (nimonic) substrate[7]. The Ni plating on the Cu substrate is very effective for preventing the Cu diffusion and producing films with nearly the same superconducting properties as those of films on nimonic[7]. The Ag plating could not prevent the Cu diffusion into the YBaCuO film. We are testing the Pt plating. The YBaCuO film on Ag shows good superconducting properties. If we use the Cu substrate, the Ag plating after Ni plating may be necessary to improve the RF surface resistance. **Fig. 5** shows the relationship between YBaCuO films and substrates (or buffer layers for the Cu substrate).

5. Surfaces of YBaCuO films

Fig. 6 (a) shows the Auger spectrum for the mechanically-polished surface of the YBaCuO film by the low-pressure plasma spraying. Any chemical polishing is not done. The spectrum shows no contamination except for the very small amount of carbon. Furthermore, the surface compositions of YBaCuO films didn't change even after heating it at 200°C for 2 hours in ultrahigh vacuum as shown in **Fig. 6** (b). The pressure of the vacuum chamber slightly increased from 5×10^{-9} Torr to 1×10^{-8} Torr. When the sintered bulk YBaCuO, on the other hand, was heated in ultrahigh vacuum chamber, the pressure increased suddenly to 10^{-6} Torr. **Fig. 7** (a, b) show the depth profiles of YBaCuO film before and after heating it in ultrahigh vacuum. The compositions of the film showed no change into about 10,000 Å in depth, and the film kept $Tc \simeq 90$ K after heating.

This means that the YBaCuO film don't release oxygen even though it is heated at 200°C in vacuum. These results contrast with the sintered bulk YBaCuO to decrease oxygen content after heating in vacuum.

It is important to study the microscopic surface structures to have a great influence upon RF superconducting properties such as field and temperature dependences of surface resistances. In order to realize some inherent potential advantages of the high Tc

films on metal substrates, we will pursue the surface improvements including methods for producing high-quality films.

6. Secondary electron emission of YBaCuO film

We have applied a scanning Auger electron microscopy to measure the secondary electron coefficient (δ) for the YBaCuO film. We have reported the secondary electron emissions for Nb[9] and Cu[10] with the same experimental apparatus. The secondary electron emission depends on surface morphology and compositions. The scanning Auger electron microscopy can measure the SEM image and Auger spectra in situ. The appratus (PHI, Model 660) at NRIM as shown in **Fig. 8** was used in this work.

Fig. 9 (a, b) show the SEM photographs of the as-sprayed and slightly mechanical polished YBaCuO films on Ag substrates with the low-pressure plasma spraying. The surface of the sprayed film was rougher than that of the sputtered film. However, a mirror-like surface of the sprayed film was obtained after careful mechanical polishing.

Fig. 10 (a ~ c) show the Auger spectra from as-sprayed, Ar^+-sputtered and air-exposed surfaces of the YBaCuO film. The clean surface after Ar^+ sputtering was exposed to air at 1 atm for 10 min. The Auger spectrum shows no contamination even after exposure to air as shown in **Fig. 10** (c). In contrast with the stable surface of the YBaCuO film, the clean surfaces of Nb and Cu metals were very active and adsorbed the carbon and oxygen remarkably after exposure to air[9)10)]. The surface of the YBaCuO film is so stable that it is hard to be contaminated even after air exposure and mechanical polishing.

Fig. 11 (a ~ c) show the secondary electron coefficients from the YBaCuO films. The surface smoothing of the plasma sprayed film was effective in suppressing the electron emission from the clean YBaCuO surface as shown in **Fig. 11** (a). The values of δ from the contaminated (as-received) surface were smaller than those from the clean surface as shown in **Fig. 11** (b). When the clean surface after Ar^+ sputtering was

exposed to air, the values of δ decreased slightly as shown in **Fig. 11** (c). The values of δ from the Nb and Cu surfaces after exposure to air were also smaller than those from the clean surfaces[9)10)]. The decreasing of these δ values is attributed to the adsorbed carbon on the surfaces[9)].

The YBaCuO films on metal substrates show the following properties.

(1) High density (no porosity) – No outgassing in ultrahigh vacuum and high Jc.

(2) Smooth and glossy for the sputtered film. Mechanical polishing is necessary for the sprayed film.

(3) Clean and stable surface – The films keep clean even after air exposure and mechanical polishing.

(4) Thermal stability.

The comparison between sintered bulk ceramics and thin films of YBaCuO is made in **Fig. 1**.

7. Summary

In our experiments, we obtained some promising results to apply the stable YBaCuO film to an RF cavity. We adopted the low-pressure plasma spraying as a suitable method for making the complete high Tc RF cavity. We are now fabricating the fully high Tc superconducting RF cavity made of the YBaCuO film inside the 3 GHz TE_{011} mode Cu cavity. This cavity will be successfully accomplished in the near future. The detailed cavity fabrication method and the RF property will be published elsewhere.

Many problems are still to be solved to obtain high performance for the high Tc superconducting RF cavity. One of the most important subjects is to achieve sufficiently low surface resistances at surface fields as high as a few hundred gauss. We will investigate the influence of microscopic surface structures on RF superconducting properties of the high Tc films. Another method to form high Tc films on large surface areas and complicated shapes of high thermal conducting metal substrates is also under the investigation. We are now also trying Pb-doped BiSrCaCuO and Tl/BaCaCuO films

to have some inherent advantages over YBaCuO type superconductors.

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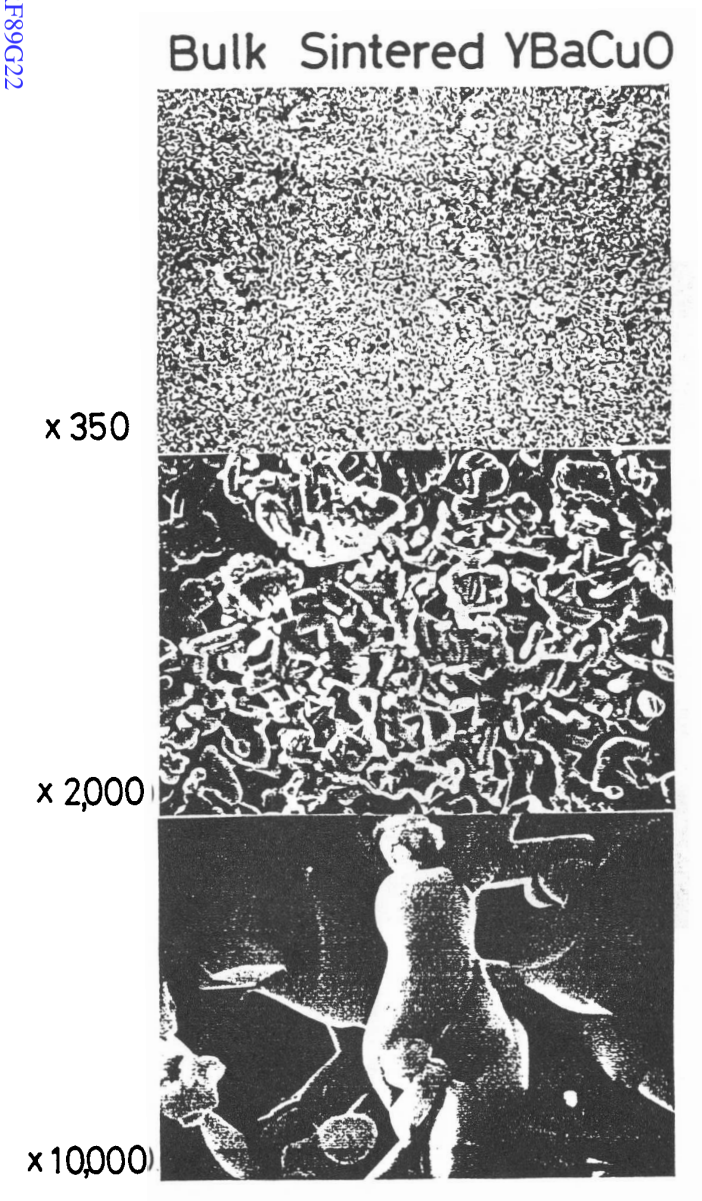
Table 1 Sputtering conditions

target	YBaCuO 2 inchϕ
substrate	Cu, Ag, SUS304, Nb, Al_2O_3, glass etc.
base pressure	2 ~ 4 x 10^{-6} Torr
substrate temp.	ambient or 400°C
sputtering gas	Ar + O_2, Ar only
sputtering pressure	~ 8 x 10^{-3} Torr
growth rate	~ 170 Å/min
RF input power	100 W ~ 150 W



RF Magnetron Sputter

Low-pressure plasma spray

Bulk sintered ceramics	Thin film on Cu, Ag
very porous	high density
low thermal conductivity	thermal stability
rough	smooth, glossy
low J_c	high J_c

Fig. 1 Comparison between bulk sintered ceramics and thin films of YBaCuO.

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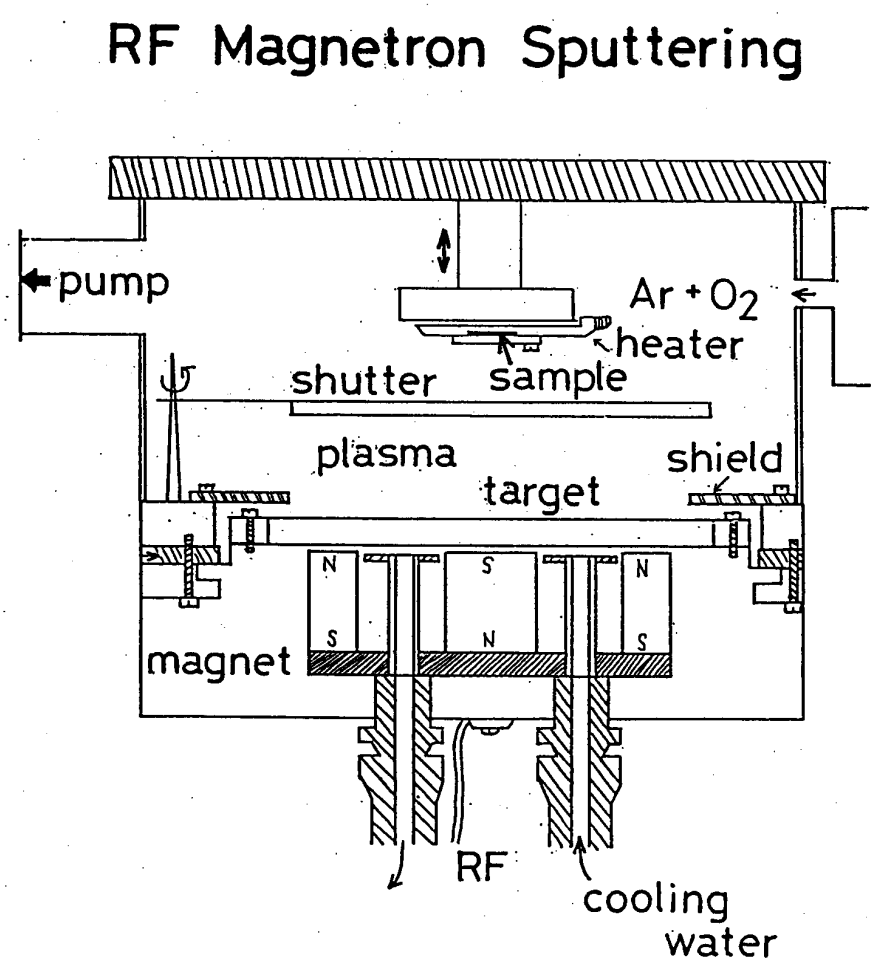


Fig. 2 Schematic diagram of RF magnetron sputtering.

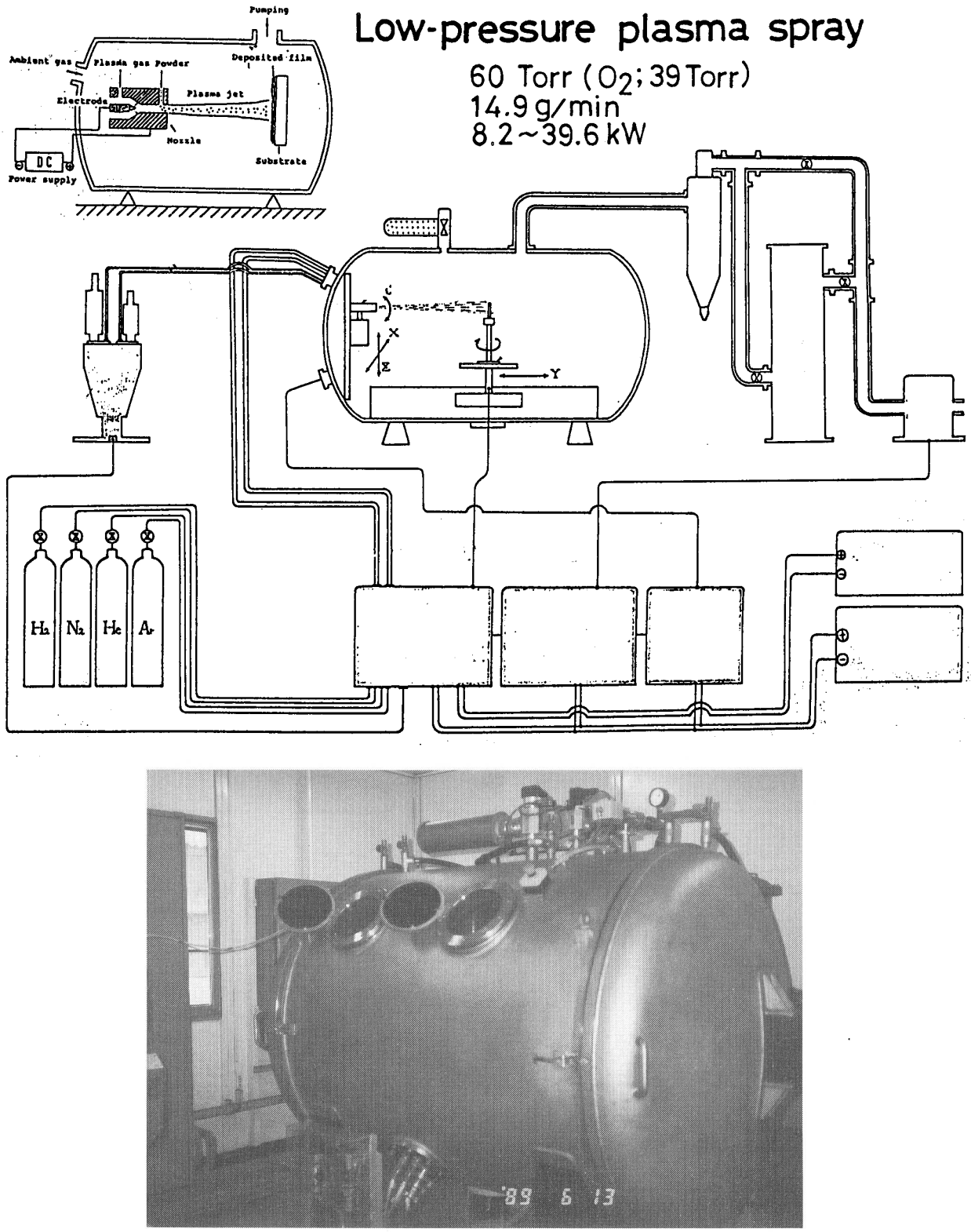


Fig. 3 Schematic diagram of low-pressure plasma spraying.[7)]

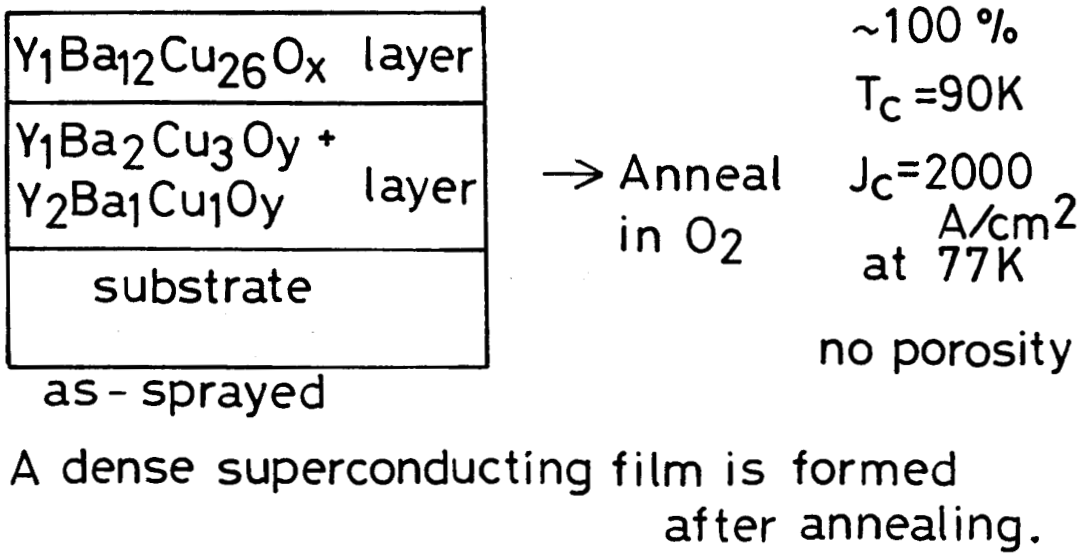


Fig. 4 Flux method with low-pressure plasma spraying.[8)]

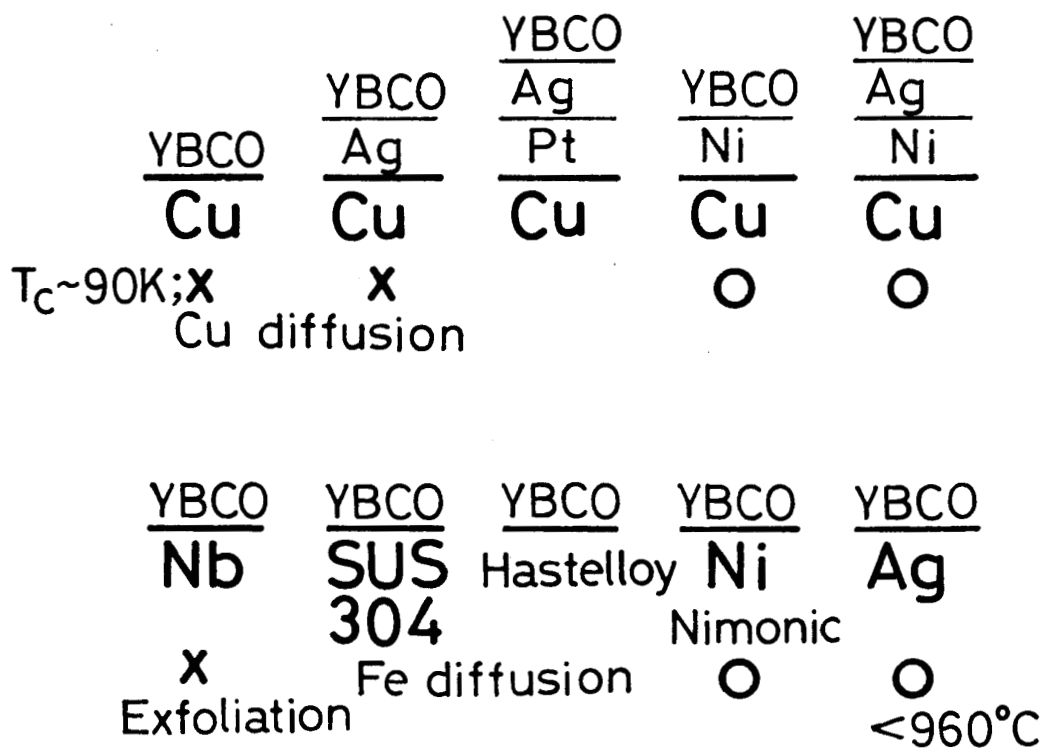
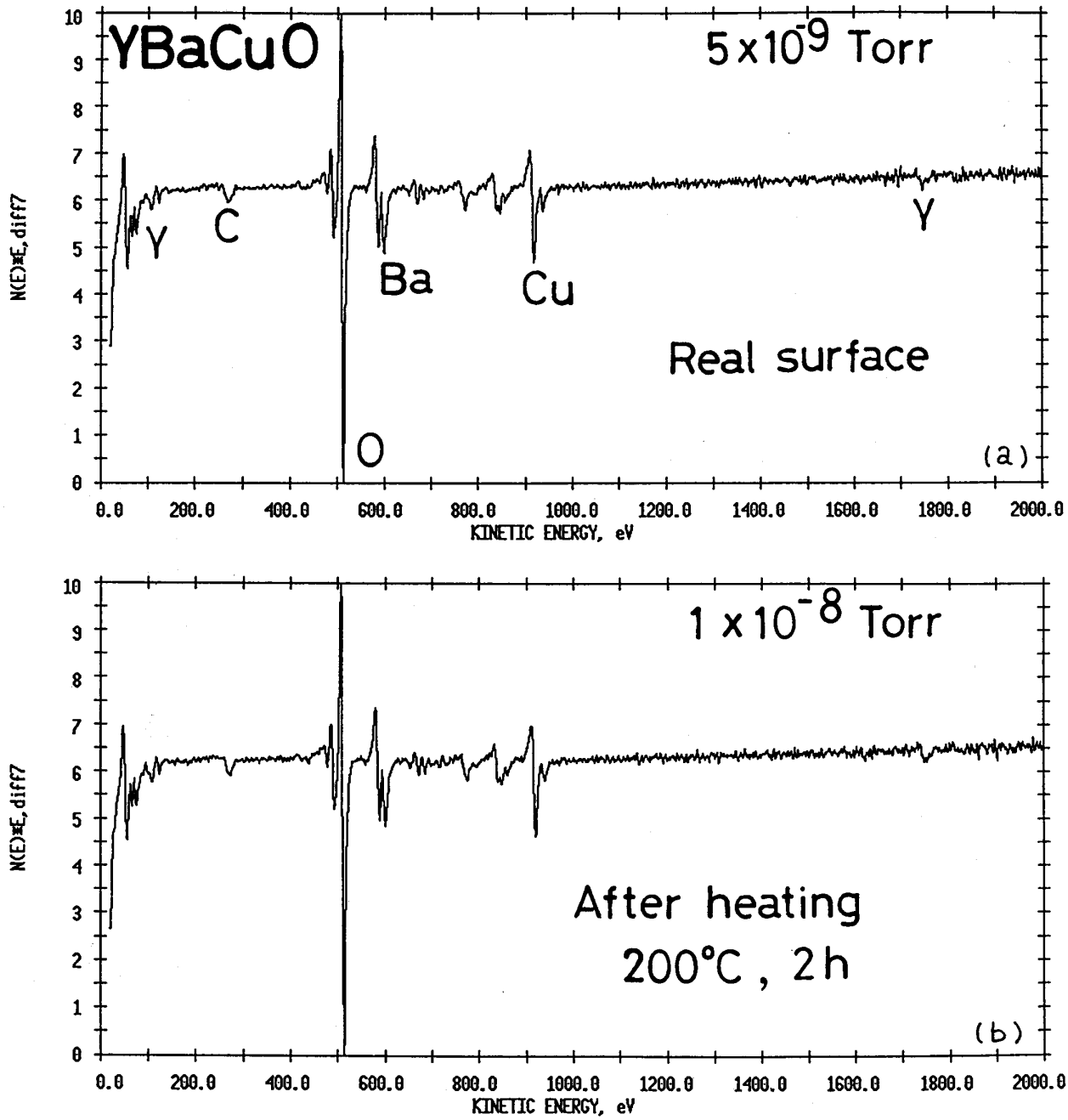
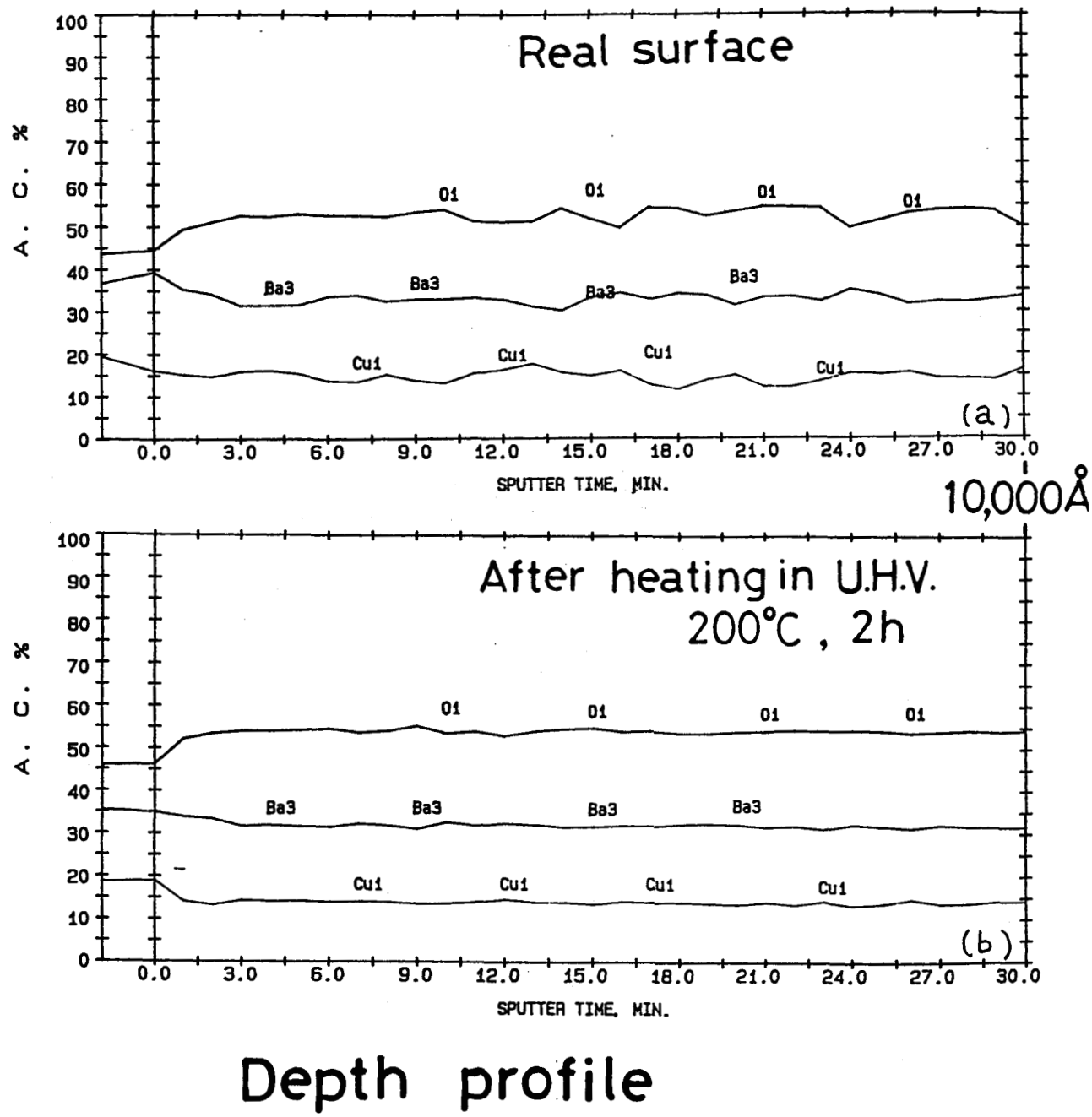


Fig. 5 Relation between YBaCuO films and metal substrates.



Auger spectra

Fig. 6 Auger spectra of YBaCuO film before (a) and after heating at 200°C for 2 hours in ulrahigh vacuum (b).



Depth profile

Fig. 7 Auger depth profiles of YBaCuO film up to 10,000 Å before (a) and after heating (b).

Scanning Auger Electron Microscopy

Secondary electron coefficient(δ) depends on surface morphology and compositions.

surface

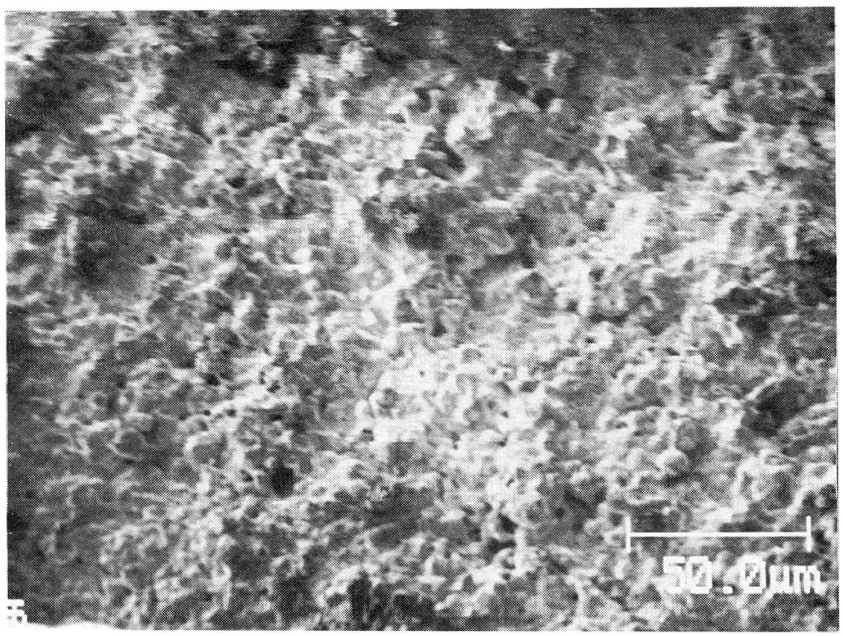
morphology → SEM image

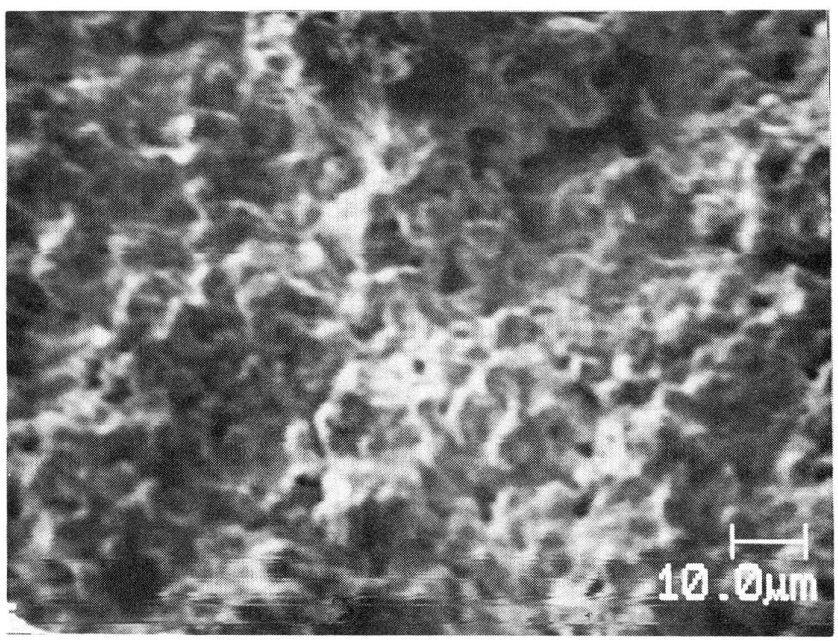
composition → AES spectra

⇩

δ

Fig. 8 Measurements of secondary electron emission with scanning Auger electron microscopy.



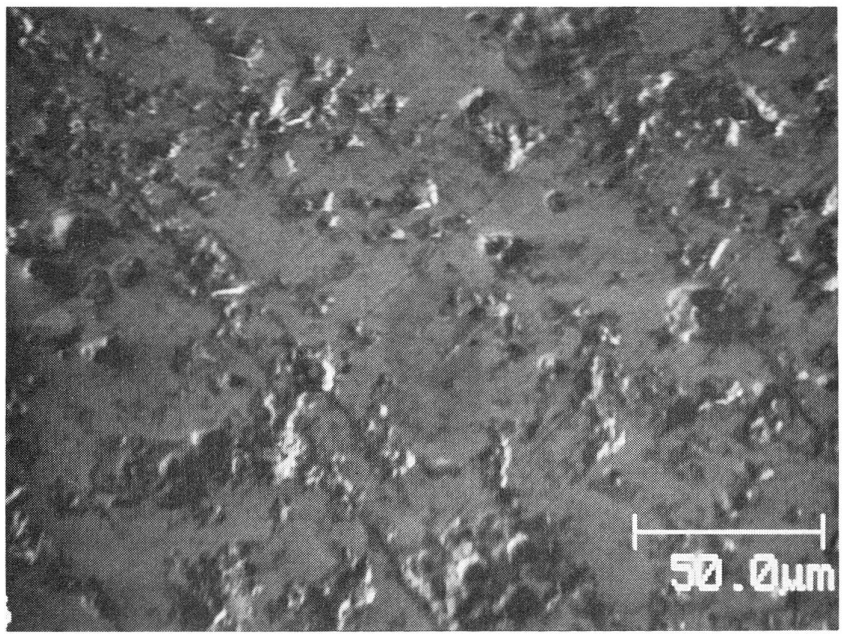


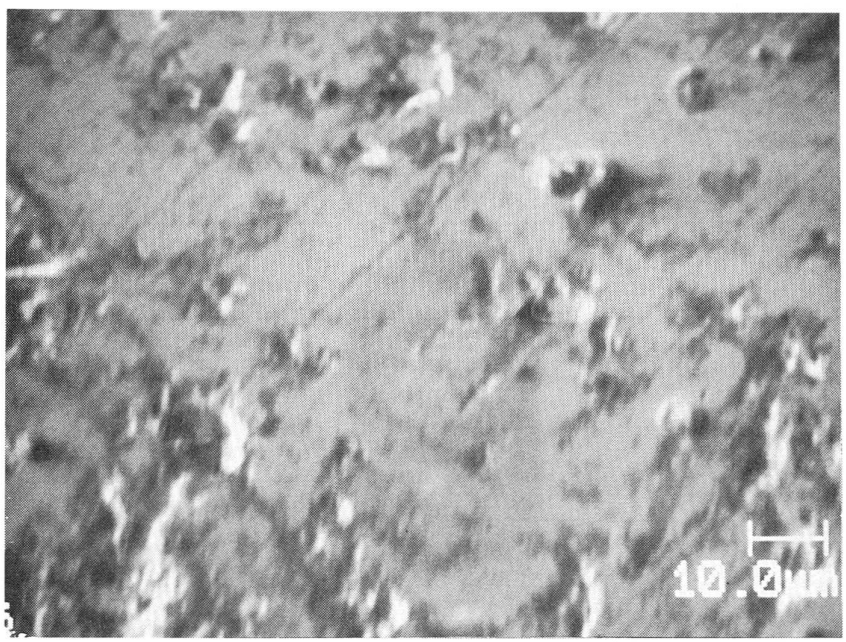
as-sprayed

YBaCuO film on Ag substrate

Fig. 9 SEM photographs of YBaCuO film on Ag substrate.

(a) as-sprayed





slightly mechanical polished

(b) slightly mechanical polished.

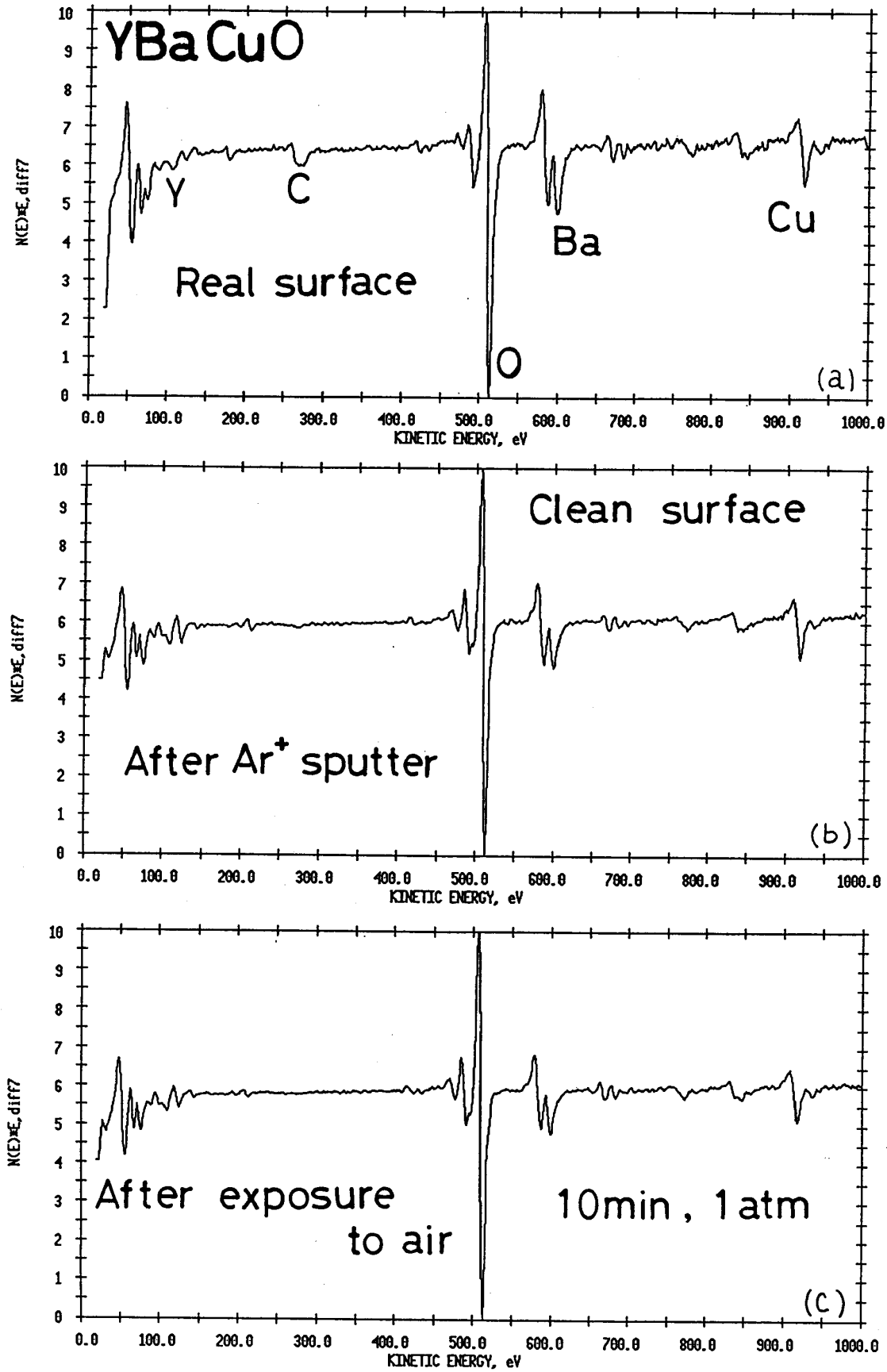


Fig. 10 Auger spectra of YBaCuO film on Ag substrate.

(a) as-sprayed (b) Ar+ sputtered (c) exposed to air

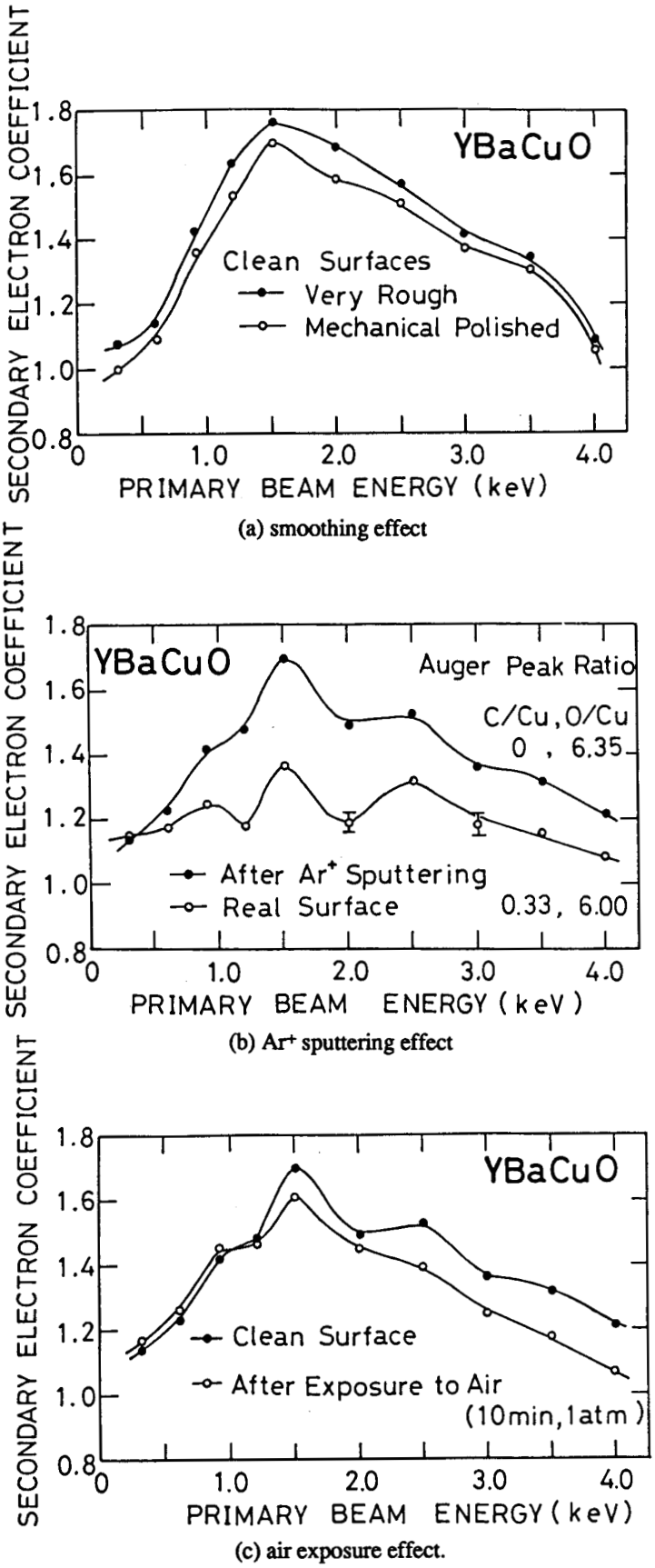


Fig. 11 Secondary electron emission data of YBaCuO film on Ag substrate.