

UV-LIGHT IRRADIATION EFFECTS ON OXIDE SUPERCONDUCTING THIN FILMS

A.Enokihara, S.Kohiki, H.Higashino, K.Setsune and K.Wasa

Central Research Laboratories,
Matsushita Electric Industrial Co., Ltd.,
Moriguchi, Osaka 570, JAPANAbstract

$\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$ thin films prepared on (100) MgO substrates by rf magnetron sputtering were irradiated with ultra-violet (UV) light in He gas of about 500 Pa using a low pressure mercury lamp. The zero-resistance temperature and the critical current density were gradually decreased with irradiation time. X-ray photo-emission spectra showed that the mean Cu valence of the film was decreased approximately from +2 to +1 by the irradiation while the valence of Bi ions was not changed. These imply that the UV light irradiation selectively reduces Cu ions and the superconductivity strongly depends on the Cu valence.

Introduction

Irradiation effects on oxide superconductors with several kinds of energy beams have been investigated from the standpoints of both study of physical properties of the materials and establishment of processing techniques for their device application.¹⁻⁶

Photon irradiation induces photo-chemical reactions in the materials. The resulting radiation effects must be primarily based on change in the bonding states. The superconductivity is known to be significantly related with the chemical states for the cuprate superconductors. In contrast to that, irradiation with heavy particles, such as ions¹ and neutrons², in many cases damages the crystal structure mechanically to create lattice defects and, in an excessive case, to form an amorphous phase. Therefore, the photon irradiation technique is effective for study of the relation between electronic states and the superconductivity in these materials. The excitation energy of electrons in the Cu 3d-O 2p bonding orbital to the upper continuous level corresponds to photon energy of UV light. Irradiation with UV-light photons is expected to effectively change the Cu-O bonding state and to induce significant effects on the superconductivity.

In this work, $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$ superconducting thin films were irradiated with UV light and the effects on the electrical properties and the chemical state were investigated.

Film preparation

$\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$ superconducting thin films of 110-nm thickness prepared on (100) MgO single-crystal substrates by rf magnetron sputtering were used in these experiments. The sputtering target of 100-mm diameter was made of a mixture of Bi_2O_3 , SrCaO_3 , CaCO_3 and CuO with a composition ratio of (Bi : Sr : Ca : Cu =) 2.1 : 1 : 0.5 : 1 sintered in air at 820 °C for 5 hours. The target-to-substrate distance was set at 25 mm. The substrate was heated at 580 °C and an rf input power was 150 W during the deposition. Sputtering gas was a mixture of 20 % argon and 80 % oxygen and total pressure was 0.5 Pa. After the deposition of 10 minutes, annealing at about 650 °C was performed in situ for 15 minutes in pure oxygen gas of more than 100 Pa. It was confirmed that the c-axis was highly oriented perpendicular to the film surface from the X-ray diffraction (XRD) analysis. The atomic ratio of the deposited film was determined to be 2:2:1:2 within an accuracy of 10 % by inductively coupled plasma emission spectrometry.

An optical absorption spectrum of the film is

shown in Fig.1. The spectrum has a broad peak at around 250-nm wavelength. The peak must be due to the excitation of electrons in the Cu-O bonding orbital because the energy for the excitation of these electrons to the upper continuous level is estimated at a few electron-volt, which corresponds to photon energy of UV light at around 250-nm wavelength. The Cu-O bonding state is expected to be effectively changed by the UV-light irradiation.

Examination of radiation effectsTransport measurement

A low pressure mercury lamp (VUV-163 manufactured by ORC), which emits the most intense radiation at 253.7 nm wavelength, was employed in the irradiation experiments for the $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$ films. The film samples were set in flowing He gas of about 500 Pa to eliminate the creation of ozone around the sample since ozone oxidizes the film surface to induce unexpected influence. A radiation power at a sample holder was measured to be about 3 mW/cm² with an optical power-meter. The sample holder was cooled at about 10 °C. The film was patterned to a Dayem-bridge shape with minimum width of 10 μm by Ar ion-beam etching for the accurate measurement of the critical current density. A standard four-probe method was employed for the measurement with electrodes of Au metal evaporated on the film surface. Figure 2 presents changes of zero-resistance temperature (T_c), critical current density at 4.2 K (J_c) and resistance at room temperature (R) of the film as functions of UV-light irradiation time. The J_c was calculated by dividing the critical current by the minimum cross section area of the film. It is apparent that the irradiation degraded the superconducting properties. The J_c was exponentially decreased with the irradiation time and, after irradiation of 70 minutes, became less than a twentieth of that before irradiation. The decrease of the T_c was not so remarkable compared to that of the J_c . Since the absorption

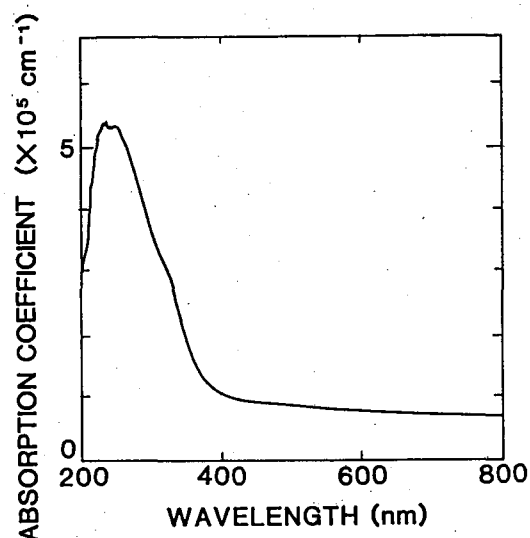


Fig.1. Optical absorption spectrum of the $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$ superconducting thin film.

Manuscript received September 24, 1990.

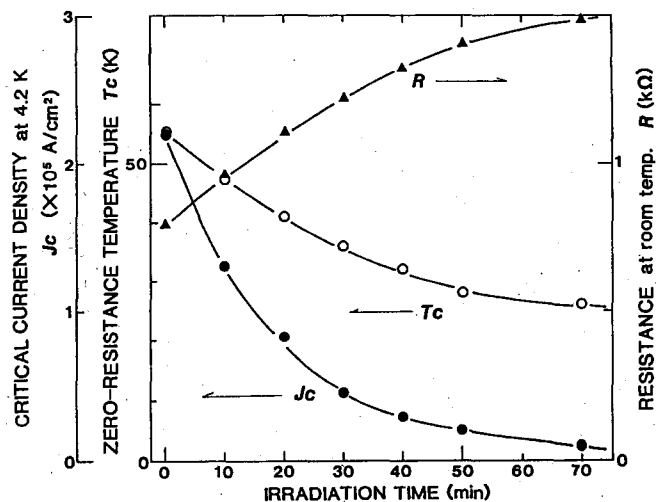


Fig.2. Zero-resistance temperature (T_c), critical current density at 4.2 K (J_c) and resistance at room temperature (R) of the $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$ thin film as functions of UV light irradiation time.

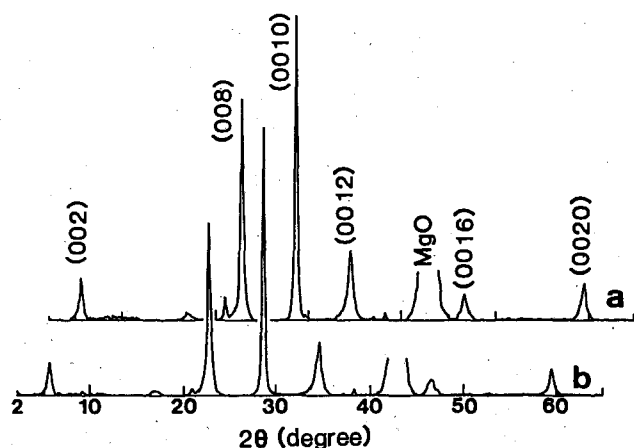


Fig.3. X-ray diffraction (XRD) patterns of the $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$ thin film, before irradiation (a) and after UV light irradiation for 5 hours (b).

coefficient of the film material is considerably large at around 250-nm wavelength as seen from Fig.1, intensity of the incident UV light should be quickly attenuated as an exponential function with the depth in the film. Therefore, the radiation damage gradually extended from the surface into the film material so that the effective thickness for the superconducting current might be exponentially decreased with the irradiation time.

X-ray diffraction

Figure 3 shows the XRD patterns for the film before and after the UV-light irradiation of 5 h. No remarkable change in the crystal structure causing the radiation damage was observed in these patterns. The damaging mechanism by the irradiation must have no relation with change in the crystallinity of film material.

X-ray photoemission spectroscopy

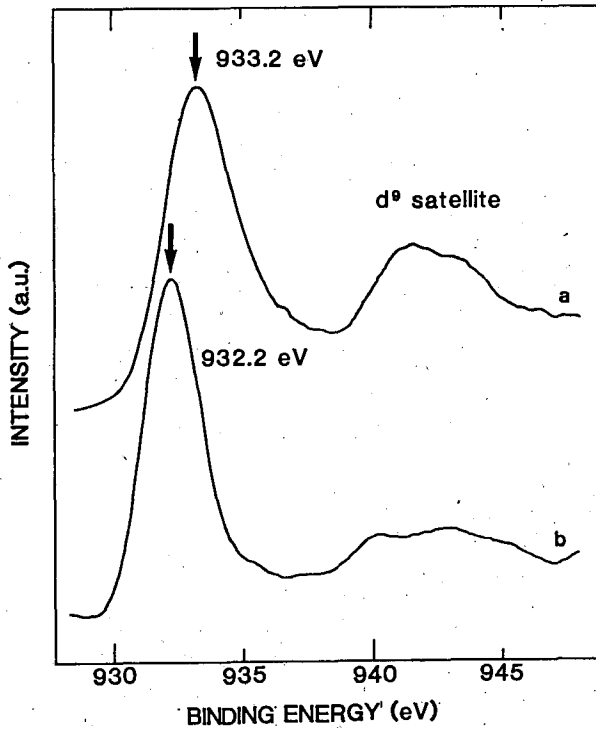
We examined radiation effects on the chemical states of the film surface by the X-ray photoemission spectroscopy (XPS). A VG Scientific ESCALAB-5 electron spectrometer with Al $K\alpha$ radiation was used to observe photoelectron spectra. An electron energy uncertainty was about 0.1 eV and an operation vacuum pressure was less than 3×10^{-8} Pa in these measurements. The film surfaces were scraped in situ by a diamond file until no further change in photoelectron spectra was observed.

The energy spectra of Cu $2p_{3/2}$ electrons of the $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$ films are shown in Fig.4(A). Curves a and b correspond to the spectra before and after the UV-light irradiation, respectively. The binding energy of Cu $2p_{3/2}$ electron was decreased from 933.2 eV to 932.2 eV after the irradiation, which shows the decrease of the mean Cu valence because the greater electron binding energy corresponds to the greater Cu valence in the oxide superconductors. The energy value of the main peak in the curve a is close to the binding energy, 933.3 eV, in $\text{Cu}^{2+}\text{-O}^{2-}$ of cuprate superconductors. The d^9 satellite peak is remarkably observed in the curve, which shows that Cu^{2+} species dominantly existed and that the charge transferred between Cu and O ions in the film before irradiation.⁷ This means that the mean Cu valence was about +2 before irradiation. On the other hand, the curve b has a narrower main peak located at 932.2 eV, which is almost equal to the binding energy in Cu_2O .⁸ From the peak width and the binding energy, the Cu valence of the irradiated film is estimated at dominantly +1. The mean Cu valence was found to be decreased approximately from +2 to +1 by the irradiation. The reduction of Cu ions would be caused by oxygen deficiencies in Cu-O layers which occurred from the photo-chemical process with UV light. Figure 4(B) shows energy spectra of Bi $4f_{7/2}$, $5/2$ electrons of the same films, where curves a and b are for films before and after irradiation, respectively. It is apparent that the irradiation made no change in the valence of Bi ions.

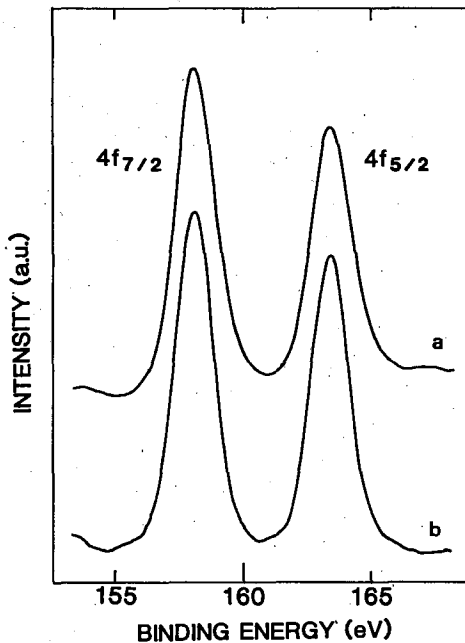
It is seen from the XPS analyses that the UV-light irradiation selectively changes the Cu-O bonding state to reduce the Cu ions and that the irradiation has no effect on the chemical state of Bi-O bonds. It is widely believed that the Cu valence not less than +2 is required for the superconductivity in the cuprate materials with hole carriers. Decrease in the Cu valence must cause the radiation damage in superconductivity. On the other hand, the valence of Bi ions was not changed in spite of the remarkable damage of the superconductivity. This must mean that the bonding state of Bi ions primarily has little relation with the superconductivity in the Bi systems.

Oxidation effects on irradiated film

If the degradation of the superconductivity is caused by the reduction of Cu ions in the irradiated film, the superconductivity will be improved to the initial state by an adequate treatment to oxidize the Cu ions. An annealing treatment in flowing oxygen at 700 °C for 2 h was performed for the film damaged by the irradiation of 3 h. The annealing at such temperature results in oxygen doping into the $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$ film material without change in crystallinity. Figure 5 shows the temperature dependence of resistivity of the film before irradiation, after irradiation and after oxygen annealing. The zero-resistance state disappeared after the irradiation and the resistivity at 273 K was increased to more than seven times that before irradiation. The T_c and the resistivity after the annealing were almost revived to those before the irradiation. The oxidization treatment fully canceled the radiation effects on the superconductivity. The



A



B

Fig.4. Photoemission spectra on Cu $2p_{3/2}$ electrons (A) and Bi $4f_{7/2}$, $5/2$ electrons (B) in the $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$ film. Curves a and b correspond to spectra of the film before and after UV light irradiation for 5 hours, respectively.

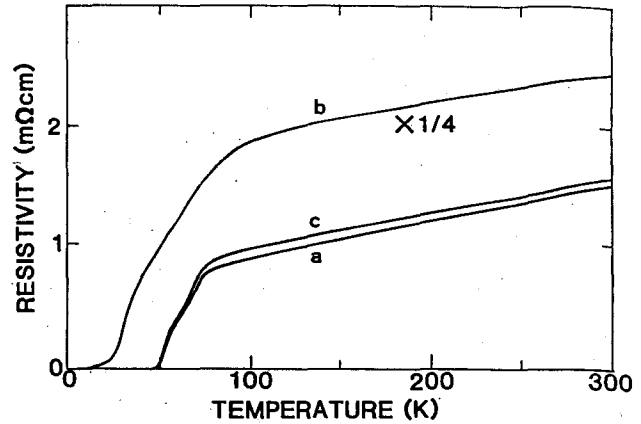


Fig.5. Temperature dependence of resistivity of the $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$ thin film before irradiation (a), after UV light irradiation for 3 hours (b) and after oxygen annealing at 700°C for 2 hours (c).

reduction of Cu ions by the UV-light irradiation must be the main cause of the degradation in the superconductivity.

Conclusion

It was found that the UV-light irradiation decreased the mean Cu valence from about +2 to +1 for $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$ films and the superconductivity was degraded while the Bi valence was not changed by the irradiation. Cu-O bonds in these oxide superconductors are known to be covalent because of the strong Cu $3d$ -O $2p$ hybridization.⁹ Electrons in the Cu-O bonding orbital will be excited to the upper continuous level by irradiation of UV-light photons at or more than about 250-nm wavelength when the photo-chemical reaction takes place in the materials. Vacancies can be induced at the oxygen sites in the Cu-O planes since the oxygen atoms would remove from their original sites and the excited electrons might be relaxed to locate on the Cu sites. Formation of the oxygen vacancies corresponds to decreasing the Cu valence and causes damage of the superconductivity. The UV-light photons, however, would not effectively excite electrons in the Bi-O bonding orbital so that no change in the Bi valence could be induced by the irradiation.

On the other hand, cations are primarily fixed on their original sites as shown from the XRD analysis. Energy of the UV-light photons would be too little to induce the removal of cations and destruction of the crystal structure.

If a usual photolithographic technique is used to irradiate the surface of a superconducting thin film with UV light, it will be possible to selectively control its superconductivity with high resolution. This may be an effective process for fabrication of high- T_c superconducting devices.

Acknowledgments

The authors wish to thank Dr. T. Nitta for his continuous encouragement.

References

1. G.J.Clark, F.K.LeGoues, A.D.Marwick, R.B.Laibowitz, and R.Koch, "Ion beam amorphization of $\text{YBa}_2\text{Cu}_3\text{O}_x$ ", Appl.Phys.Lett., 51, 1462-1464, 1987.
2. J.R.Cost, J.O.Willis, J.D.Thompson, and D.E.Peterson, "Fast-neutron irradiation of $\text{YBa}_2\text{Cu}_3\text{O}_x$ ", Phys.Rev. B-37, 1563, 1988.
3. M.Nastasi, D.M.Parkin, T.G.Zocco, J.Koike, and P.R.Okamoto, "Electron irradiation induced amorphization in $\text{YBa}_2\text{Cu}_3\text{O}_7$ and $\text{GdBa}_2\text{Cu}_3\text{O}_7$ superconductors", Appl.Phys.Lett. 53, 1326-1328, 1988.
4. J.Bohandy, J.Suter, B.F.Kim, K.Moorjani, and F.J.Adrian, "Gamma radiation resistance of the high T_c superconductor $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ ", Appl.Phys.Lett. 51, 2161-2163, 1987.
5. A.Enokihara, S.Kohiki, K.Setsune, K.Wasa, Y.Higashi, S.Fukushima, and Y.Gohshi, "X-ray irradiation effects on $\text{ErBa}_2\text{Cu}_3\text{O}_{7-x}$ superconducting thin films", Physica C, 161, 431-434, 1989.
6. H.Tamura, A.Yoshida, S.Morohashi and S.Hasuo, "Ozone-UV irradiation effects on $\text{Ba}_2\text{YCu}_3\text{O}_{7-x}$ thin films", Appl.Phys.Lett. 52, 2183-2185, 1988.
7. L.Yin, I.Adler, T.Tsang, L.J.Matienzo and S.O.Grim, Chem. Phys.Lett. 24 (1974) 81.
8. T.L.Barr, "ESCA study of the termination of the passivation of elemental metals", J.Phys.Chem. 82 (1978) 1801.
9. S.Kohiki, S.Hayashi, H.Adachi, S.Hatta, K.Setsune and K.Wasa, "Electron spectroscopy of $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_{4-y}$ ($x=0, 0.15$ and 0.23) thin films", J.Phys.Soc.Jpn. 58 (1989) 4139.