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To cite this article: H Tada et al 2009 J. Phys.: Conf. Ser. 150 052255

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Preparation of n-type YBa$_2$Cu$_3$O$_y$ films by an electrochemical reaction method

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Abstract. We report on the continuous carrier control from holes to the electrons in YBa$_2$Cu$_3$O$_y$ (YBCO) films by an electrochemical reaction method. In this method, the reduction in the hole concentration or the electron doping occurs at room temperature simply by applying a voltage of ∼1 V between the YBCO film and the Pt electrode in the electrolyte solution of AClO$_4$/polyethylene oxide, where A = K or Cs. When the initial sample is slightly overdoped, a dome-like increase and decrease of $T_c$ and an increase of resistance $R$ and Hall coefficient $R_H$, which correspond to a reduction in the hole concentration to ∼10$^{21}$ cm$^{-3}$, are observed with increasing voltage or application time. These results suggest that this electrochemical method is a straightforward and effective method for electron doping. Starting with a heavily underdoped sample, which is not superconductive, we succeeded in changing the sign of $R_H$ from positive to negative and in rapidly reducing $R$.

1. Introduction

The carrier concentration and its sign have been key parameters in controlling the properties of high-$T_c$ cuprate superconductors for long time. It is well known that the superconductivity in cuprates can be achieved by doping the Mott-insulating state with either holes ($p$-type carriers) or electrons ($n$-type carriers). However, $p$-type and $n$-type cuprates differ in their doping dependences of magnetic and superconducting transition temperatures and in their crystal structures [1]. It is not so clear whether this hole-electron asymmetry is inherent or not. In order to resolve this question, it is desirable either to develop a method for continuously converting a carrier from a hole to an electron or to find a crystal system in which it is possible to change the sign of a carrier [2].

Recently, a new carrier control method that employs an electrolyte in a field-effect transistor (FET) structure has been attracting growing interest [3-7]. In this structure, a voltage applied between two electrodes causes a counter motion of the ions in the electrolyte toward the corresponding electrodes. When one of the electrodes is the sample for control, two different phenomena are expected to occur near the sample surface; which phenomenon occurs depends on the nature of the sample. When no electrochemical reaction occurs, the ions approaching the sample surface form an electric double layer (EDL), which functions as an effective gate capacitor [7]. The accumulation of surface carriers generated by this EDL capacitor is a more effective method for achieving reversible carrier control with FET structures than the conventional metal-insulator-semiconductor FET method [8, 9]. On the other hand, when, as is the case in this study, an electrochemical reaction (e.g., intercalation or deoxidization) occurs between the sample and the electrolyte, applying a voltage accelerates the chemical reaction. For high-$T_c$ cuprates this phenomenon may be used as a straightforward and
effective way of controlling the carriers. Since this electrochemical reaction occurs at room temperature, we expect the strong doping effect, which is not possible using the conventional method involving heat treatment.

In this work, we used the above-mentioned electrochemical method to control the carrier concentration in YBa$_2$Cu$_3$O$_y$ (YBCO) films over a wide range to the extent that the sign of the charge carriers changes. In addition to confirming the strong electron doping effect on $T_c$, we succeed in obtaining $n$-type YBCO. The reaction in the film samples is discussed.

2. Experimental

YBCO films typically 50 nm thick were grown by RF magnetron sputtering on SrTiO$_3$ (100) single crystal substrates at 800°C [10]. As the starting materials, we prepared slightly-overdoped and heavily-underdoped YBCO films, the doping levels of which were tuned by the oxygen partial pressure during cooling (1 atm for the slightly-overdoped samples and $5 \times 10^{-4}$ atm for the heavily-underdoped samples) after deposition. The films were patterned into a Hall geometry (dimensions: 200 (length) x 200 (width) μm$^2$) by using photolithography techniques. Cu leads were bonded to the sample and then the sample and the Pt electrode above the sample were immersed in the electrolyte AClO$_4$/PEO (where A = K or Cs; PEO: polyethylene oxide) with mixing ratios of [O]/[K] = 20 or [O]/[Cs] = 40.

We performed repeated measurements of the temperature dependence of the resistance $R(T)$ with decreasing $T$ and the field dependence of the Hall coefficient $R_H(H)$ from $H = 5$ to -5 T at 100 K after applying the voltage $V_g$ between the YBCO film and the Pt electrode for 1-2 h at 300 K. A temperature of 300 K was selected since ionic motion almost ceases below 280 K due to the glass transition of PEO. Here, the positive $V_g$ causes the A$^+$ and ClO$_4^-$ ions to move to the YBCO film and Pt electrode, respectively, resulting in the electron doping of YBCO.

3. Results and discussion

Figure 1 shows the typical variation of $R(T)$ with positive $V_g$ in KClO$_4$/PEO when the initial sample is slightly-overdoped. We observed an increase of $R$ of this sample with increasing $V_g$, so that it became almost 10 times larger value at $V_g = 3.0$ V than the as-grown sample. With increasing $V_g$, the superconducting transition temperature $T_c$ first increases, peaking at around $V_g = 1$ V, and then decreases. This dome-like variation in $T_c$, together with the increase in $R$, reminds us of the reduction in the hole concentration from the overdoped region to the underdoped one by passing through the optimal point. Indeed, an increase in $R_H$ with $V_g$, which corresponds to the reduction in the carrier density $n$ ($\equiv 1/eR_H$) with $10^{21}$ cm$^{-3}$V$^{-1}$, is observed at 100 K. The same trends in the changes are
observed when we examine $R$ and $R_H$ as a function of the application time of $V_g$, with $V_g$ fixed at a constant value, and also for CsClO$_4$/PEO. We note that all the above changes do not recover to their initial values when $V_g$ is reduced again. This irreversibility is in contrast with the reversibility of the carrier accumulation at the sample surface using EDL-FET [7] and the reversible electrochemical reaction in electrolyte [5]. We also measured the thickness of the YBCO film, which was prepared in the same condition with the sample in figure 1, by the surface profiler and confirmed that it was unchanged after processing in the electrolyte. Therefore, our experimental process causes the electrochemical reaction to extend deep inside the film, producing a large reduction in the hole density (electron doping). A reaction to increase the number of holes was also attempted by applying a negative $V_g$. However, no significant changes in the physical quantities were observed.

Using this effective electron doping process, we tried to realize an $n$-type YBCO. Figure 2 show a plot of the sequence of $R(\theta)$ measurements at a fixed $V_g = 1.0$ V in CsClO$_4$/PEO as a function of the reaction time $t_a$ at 300 K. In this sequence we start with a heavily underdoped sample, which is already non-superconductive due to oxygen reduction in cooling process. We used X-ray diffraction to confirm that the as-grown film was highly $c$-axis oriented with a lattice constant $c = 1.183$ nm. This demonstrates that the insulating behavior observed in figure 2 is not caused by decomposition in the preparation process. $R$ increases significantly and exceeds our measurement limit when $t_a$ becomes greater than 4 h. Subsequently, $R$ starts decreasing with a further increase in $t_a$. At the same time, we observe the sign in $R_H$ changes from positive to negative value. The carrier density $n$ determined by $1/eR_H$ at 100 K crosses the line of $n = 0$ around $t_a = 4$ h and subsequently becomes negative. It continues to decrease (increase in the absolute value) with a further increase in $t_a$. These results indicate that a change from $p$-type carriers to $n$-type carriers occurs in the YBCO film with the electrochemical reaction in this study. The degree of electron doping progresses to the extent that $R$ decreases by more than two orders of magnitude at 300 K after the sign change.

Possible electrochemical reaction that could be occurring in our process are the intercalation of K$^+$ or Cs$^+$ into the YBCO or deoxidization, both of which can result in electron doping. In the former case, it is not easy to determine where the ions are intercalated. In the latter case, the detailed reaction process is unknown. Further investigation of the microstructure and sample composition is necessary.

Finally, superconductivity in $n$-type YBCO was not observed in this work. This may be due to the carrier concentration being still low. However, it should be noted the oxygen content $y$ in $n$-type YBa$_2$Cu$_3$O$_{y}$ may decrease below 6 [11]. This implies that the oxygen in the CuO chain sites almost disappears.

Figure 2. Temperature dependence of $R$ at various reaction time $t_a$ in CsClO$_4$/PEO.
4. Conclusion
An electrochemical method using an electrolyte in a FET structure is found to be an effective method of electron doping in YBCO films. Using this method, we succeeded in continuously changing $p$ type carriers to $n$ type carriers and in obtaining an $n$-type YBCO with metallic conduction.

Acknowledgements
We thank M. Kawasaki for useful discussions, and Y. Watanabe, S. Tanno, K. Hosokura, H. Miura and A. Ogata for assistance with using the low temperature apparatus.

References
[1] Tokura Y, Takagi H and Uchida S 1989 Nature 337 345
[2] Segawa K and Ando Y 2006 Phys. Rev. B 74 R100508
[3] Panzer M J and Frisbie C D 2005 J. Am. Chem. Soc. 127 6960
[4] Takeya J, Yamada K, Hara K, Shigeto K, Tsukagoshi K, Ikehara S and Aoyagi Y 2006 Appl. Phys. Lett. 88 112102
[5] Shimotani H, Diguet G and Iwasa Y 2005 Appl. Phys. Lett. 86 022104
[6] Shimotani H, Asanuma H, Takeya J and Iwasa Y 2006 Appl. Phys. Lett. 89 203501
[7] Shimotani H, Asanuma H, Tsukazaki A, Ohtomo A, Kawasaki M and Iwasa Y 2007 Appl. Phys. Lett. 91 082106
[8] Ahn C H, Triscone J-M and Mannhart J 2003 Nature 424 1015
[9] Matthey D, Reyren N, Triscone J-M and Schneider T 2007 Phys. Rev. Lett. 98 057002
[10] Kyoso T, Nojima T, Okayasu S and Kobayashi N 2004 Physica C 412-414 506
[11] Jorgensen J D, Veal B W, Paulikas A P, Nowicki L J, Crabtree G W, Claus H and Kwok W K 1990 Phys. Rev. B 41 1863