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Recovery of $YBa_2Cu_3O_{7-y}$ etched by helium ions

Yoshitake Nishi, Yasuo Takahashi, Seiichiro Takagi, Takashi Sudo, Noriyuki Inoue, and Toshio Shima
Department of Materials Science, Tokai University, 1117, Kitakaname, Hiratsuka, Kanagawa, 259-12, Japan

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It is a serious problem that excess helium-ion etching greatly decreases T_c. Thus, a recovery process is investigated for high-T_c $YBa_2Cu_3O_{7-y}$. Isothermal heat treatment recovers the T_c value for the excess etched samples, and T_c increases beyond its value before etching. The maximum value of the offset temperature increases to 94.6 K. Excess heat treatment decreases T_c. The T_c value of the excess aged sample approaches that before the etching. The apparent activation energy of the recovery process is 171 kJ/mol.

I. INTRODUCTION

Ion etching is a good tool to form ceramics precisely. Thus, we have investigated ion etching of high-T_c superconductor $YBa_2Cu_3O_{7-y}$.[1] A rapid rate of etching was found. Furthermore, the influence of argon-ion etching on T_c were studied for the high-T_c superconductor $YBa_2Cu_3O_{7-y}$.[2] Excess argon-ion etching greatly decreases the T_c value below 4.2 K. It is a serious problem. However, we found that heat treatment recovers the T_c value.[3]

We have recently found the rapid rate and a polishing effect by a helium-ion etching.[4] The greatly decreasing T_c is also found with an excess of helium-ion etching. Thus, we began the present study to observe the influence of heat treatment after excess helium-ion etching on T_c for the $YBa_2Cu_3O_{7-y}$.

II. EXPERIMENTAL PROCEDURE

Samples with nominal composition $YBa_2Cu_3O_{7-y}$ were prepared by high-purity powders of CuO (99.9%), $BaCO_3$ (99.9%), and Y_2O_3 (99.99%). The powders were mixed and reacted under pure oxygen at 1210 K for 2 h and then air cooled. After crushing, a pellet-shaped tablet, 0.8 mm thick and 13 mm in diameter, was sintered under pure oxygen at 1210 K for 8 h and then furnace cooled. The cooling rate was 4.2 K/min at 973 K.

Ion etching was performed under a 4×10^{-4} Torr helium atmosphere just above the specimen by a Kaufman-type ion milling apparatus (ISM-S, Elionix, Tokyo).[5] The energies for ion acceleration and ion current density were 1.0 keV and 0.6 mA/cm^2, respectively. The ion beam was perpendicular to the sample surface.

The electrical resistivity was measured using a standard four-probe technique and a Keithley 181 nanovoltmater. The temperature was measured by a Au-Fe-chromel thermocouple attached to the specimen in a cryostat at equilibrium temperature. The structure of the sample was monitored by x-ray diffraction (model no. Ru-200B, Rigaku Denki, Tokyo). The diffraction was performed using a step scanning method (Cu target, 40 kV, 50 mA, 0.04 deg/step, 4 s/step).

III. RESULTS

A. T_c change by recovery

Excess helium-ion etching significantly decreases T_c below 4.2 K. Heat treatment recovers the T_c value for the excess etched samples. To recover the T_c values of the excess etched sample [$T_c^0 < 4.2$ K, etching time (t_e) 3000 s, ion acceleration energy 1 keV, ion current density 0.6 mA/cm^2], heat treatment (aging) is performed in a pure oxygen atmosphere.

Figure 1 shows the temperature dependence of the electrical resistivity of the excess etched $YBa_2Cu_3O_{7-y}$ sample after heat treatment for 1500 s together with the sample before etching. The lower the temperature, the lower the electrical resistivity becomes. The offset T_c^0 of the superconducting transition is defined as the temperature corresponding to the achievement of zero resistivity (below 10^{-9} Ω m at 0.2 mA/mm^2 current density). After heat treatment for 1500 s, the T_c^0 value is 94.6 K, whereas T_c^0 is 92.0 K before etching.

The value of T_c^0 depends on a measuring current density (I). Figure 2 shows changes in the T_c^0 value against I for the excess helium-ion etched $YBa_2Cu_3O_{7-y}$ sample after heat treatment ($t_e=3000$ s, $T_h=825$ K, $t_a=1500$ s), together with the sample before etching. The solid line is

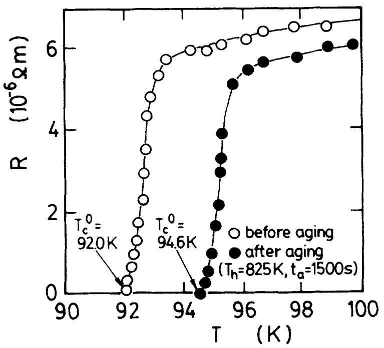

FIG. 1. The change in electrical resistivity (R) with temperature (T) of a helium-ion etched $YBa_2Cu_3O_{7-y}$ sample after heat treatment ($T_h=825$ K, $t_a=1500$ s), together with samples before etching.

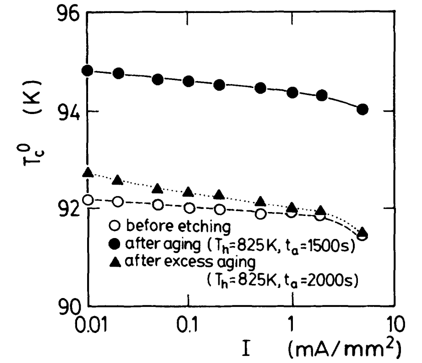

FIG. 2. The change in critical current density (I) against T_c^0 of helium-ion etched $YBa_2Cu_3O_{7-y}$ samples after heat treatment ($T_h = 825$ K, $t_a = 1500$ and 2000 s), together with the sample before etching.

for the heat-treated sample of the excess etched sample which shows the maximum T_c^0, whereas the dotted line is for the sample before the helium-ion etching. T_c^0 increases with decreasing I. The detectable T_c^0 (see solid line) is 94.8 K at 0.01 mA/mm^2 of I.

Figure 3 shows changes in the T_c^0 value against the heat-treatment time (t_a). Solid, dashed, and dotted lines are for the different heat-treatment temperatures (T_h) at 825, 775, and 725 K, respectively. Heat treatment increases the T_c value beyond that before etching. Namely, the maximum value of T_c^0 (${}^{\max}T_c^0 = 94.6$ K) is 2.6 K larger than that ($T_c^0 = 92.0$ K) before etching. Figure 4 shows the T_c^0 change against the temperature of heat treatment. The higher the temperature of heat treatment, the higher the ${}^{\max}T_c^0$ becomes. The value is much more than expected.

Excess heat treatment slightly decreases the T_c value (see Fig. 2). It approaches the value before ion etching.

B. Activation energy

Figure 5 shows the change in the heat treatment time (t_a) to the maximum T_c^0 against the reciprocal temperature of heat treatment. The apparent activation energy of the recovery process is 171 kJ/mol. It approximately

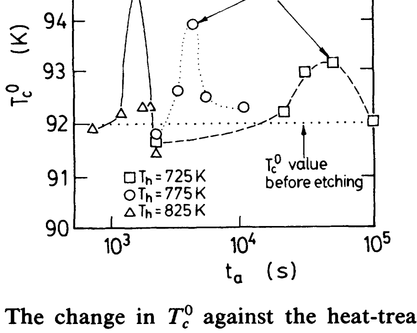

FIG. 3. The change in T_c^0 against the heat-treatment time (t_a) of helium-ion etched $YBa_2Cu_3O_{7-y}$ samples. Solid, dotted, and dashed lines are for heat treatments at 825, 775, and 725 K, respectively.

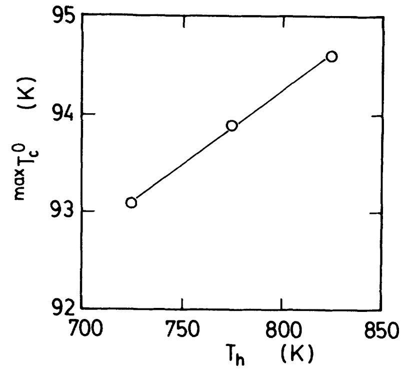

FIG. 4. The change in maximum T_c^0(${}^{\max}T_c^0$) against the temperature (T_h) of heat treatment.

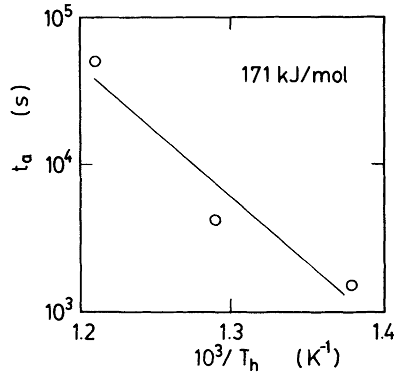

FIG. 5. The change in the heat-treatment time (t_a) to maximum T_c against the reciprocal temperature ($1/T_h$) of heat treatment of $YBa_2Cu_3O_{7-y}$ samples etched by helium ion.

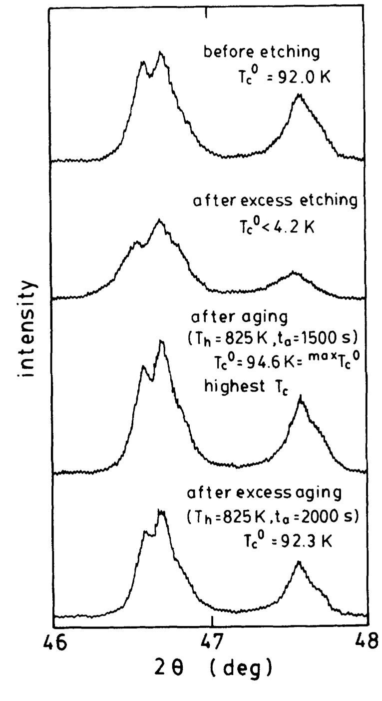

FIG. 6. X-ray diffraction patterns of $YBa_2Cu_3O_{7-y}$; before and after etching ($t_e = 0$ and 3000 s) together with excess etched and after heat-treated samples ($t_e = 3000$ s, $T_h = 825$ K, $t_a = 1500$ and 2000 s).

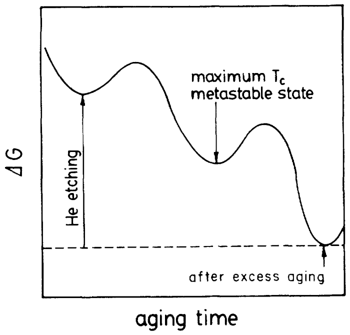

FIG. 7. The schematic diagram of the free-energy change against the heat-treatment time.

coincides with the activation energy of the diffusivity of the oxygen atom in $YBa_2Cu_3O_{7-y}$.[6]

C X-ray-diffraction pattern

Figure 6 shows x-ray-diffraction patterns of the samples before and after excess helium-ion etching ($t_e=0$ and 3000 s) together with those of the excess etched samples after heat treatment ($t_a=1500$ and 2000 s). Most peaks can be identified as an orthorombic structure, which corresponds to an oxygen-deficient perovskite.

It probably breaks Cu-O bondings more easily than Y-O and Ba-O bondings and then enhances a free energy to an unstable state (see Fig. 7) by excess etching. Excess etching increases a peak width. The larger the peak width, the lower the crystal perfection becomes. Thus, the T_c value decreases.

IV. DISCUSSION

Heat treatment approaches the samples to the equilibrium state. On the way to the equilibrium state, we suggest a metastable state at which a high-T_c phase exists (see Fig. 7). Namely, heat treatment enhances the T_c value which is 2.6 K larger than that before etching because it enhances the crystal perfection. Although the highest T_c is found in the metastable state that shows the small peak width (the highest crystal perfection; see peak at 1500 s in Fig. 6), the atom site distribution in the orthorhombic structure is not the most stable from the thermodynamics point of view. Thus, excess heat treatment approaches the equilibrium. Since excess heat treatment lowers the crystal quality, it slightly increases the peak width (see peak at 2000 s in Fig. 6). Therefore, it decreases the T_c value (see Fig. 3) and it approaches its T_c value before etching because the structure seems to be similar to that before etching (see Fig. 6).

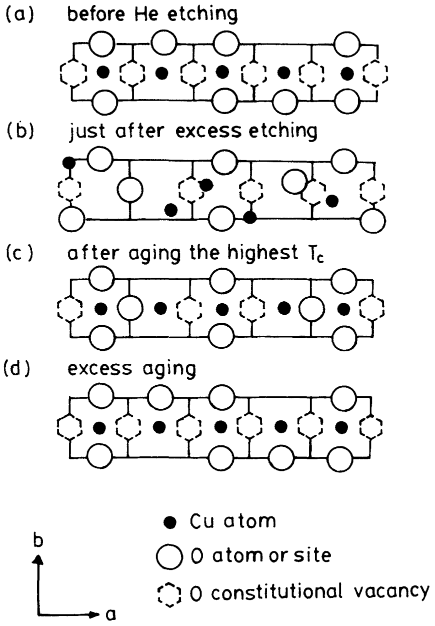

FIG. 8. The schematic structure of the *a*-*b* plane in $YBa_2Cu_3O_{6.8}$ (a) before He etching, (b) just after excess etching, (c) the highest T_c sample after heat treatment, and (d) after excess heat treatment.

If the fully oxygen content zone (see the high-angle peak of the highest T_c sample in Fig. 6) homogeneously exists, then the increase of T_c is explained. Figure 8 shows schematically the structure of the *a*-*b* plane in the $YBa_2Cu_3O_{6.8}$. Since helium-ion etching disorders the crystal structure [see Fig 8(b)], the atoms would like to move the equilibrium sites during heat treatment. On the way to the equilibrium state, we suggest that the metastable state exists. Namely, it occurs in the oxygen-rich zone which is shown in Fig. 8(c). Therefore, the time to the maximum T_c value is probably dominated by the oxygen atom diffusivity (see Fig. 5).

V. CONCLUSION

In summary, heat treatment was performed on the excess helium-ion etched sample, which shows a low T_c. Heat treatment increases the T_c value beyond the value before the etching. The maximum increased value of the offset temperature is 2.6 K. Excess heat treatment decreases the T_c value. Excess heat treatment approaches the T_c value before etching. The apparent activation energy of the recovery process is 171 kJ/mol. It agrees approximately with the activation energy of the oxygen diffusivity in $YBa_2Cu_3O_{7-y}$.

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