Superconductivity in In$_2$O$_3$-ZnO crystalline films

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**Abstract.** Thin In$_2$O$_3$-ZnO (IZO) films were prepared by DC-magnetron sputtering with changing the weight concentration $x$ of ZnO, $0 \leq x \leq 0.07$. As-grown amorphous IZO films show the metallic characteristic but do not show superconductivity. We have investigated the $T$ and $H$ dependence of the resistivity $\rho$ and Hall coefficient for annealed films with thickness $d=350$ nm in air. It is found that the films with $0 \leq x \leq 0.03$ show superconductivity. Transition temperature $T_c$ and the carrier density $n$ of these films are $\approx 2.0$ K and $10^{25} - 10^{26}$ m$^{-3}$, respectively. The annealed In$_2$O$_3$-ZnO films were examined by a high resolution transparent electron microscopy. This investigation reveals that films annealed at 300 $^\circ$C are sufficient crystalline. There is a difference of crystal structures between the superconducting film and normal film. We studied the upper critical magnetic field $H_{c2}(T)$ for the film with $x=0.005$. From the slope of $dH_{c2}/dT$, we obtain the coherence length $\xi(0) \approx 100 \text{ Å}$ at $T=0$ K and the coefficient of the electronic heat capacity $\gamma \approx 3.2 \text{ (J/m}^3\text{K}^2)$ which is small compared with that of other oxide materials.

There is a great deal of interest in the transparent electrode material, amorphous zinc-doped indium oxide(a-In$_2$O$_3$-ZnO,a-IZO) for devices such as liquid crystal displays. Some characteristics [1][2] have been investigated, however, detailed studies of the transport properties at low temperatures are few. Recently, for a-IZO films, we have examined the electrical properties at temperatures 2.0 K $< T <$ 300 K [3]. When the weight concentration $x$ of ZnO is less than $\approx 0.1$, the resistivity $\rho(T)$ of films shows the metallic characteristics, that is $d\rho/dT > 0$, at a wide temperature region. However, we do not observe superconductivity. Although the post annealing in a vacuum does not increase the resistivity, the annealing in air brings large resistivity due to depression of the carrier density. From the large difference of effects between two annealing procedures, it is expected that the annealing in air gives new transport phenomenon. As for an appearance of superconductivity, Mori reported that tin-doped indium oxide films show the sharp superconducting transition by proper annealing condition and found that the low temperature annealing brings the existence of superconductivity [4]. In this paper, we report that IZO films prepared by some annealing conditions in air show superconductivity. In order to find the correlation between the electronic transport property and the crystal structure, we investigate the film structure by the high resolution transparent electron microscopy.
At first, a-IZO films with \( d = 350 \) nm were prepared by the deposition on glass substrates by the DC-magnetron sputtering method using the ceramic oxide IZO target under 0.3 Pa of Ar. We prepared several targets with different weight concentration \( x \) of ZnO, \( x = 0.0, 0.005, 0.01, 0.02, 0.03, 0.04, 0.05 \) and \( 0.06 \). During deposition, the substrate temperature was kept at room temperature. By XRD analysis, it is recognized that these films have amorphous structure. After deposition, we annealed the films in air and in \( \text{N}_2 \) gas. For the effect of post annealing IZO films in air, it is reported that films annealed at 250 °C for 1 hour take an amorphous structure [5]. Such amorphous films do not show superconductivity but the behaviors due to localization or electron-electron effects [3]. Therefore, in order to investigate the effects of the annealing temperature \( T_a \) and annealing time \( t_a \) on superconductivity, we changed the \( T_a \) from 100 to 300 °C and \( t_a \) from 0.5 to 24 hours. Furthermore, the effect of annealing in \( \text{N}_2 \) gas at \( T_a = 300 \) °C were also investigated for In\(_2\)O\(_3\) films. As for \( x \), we found that the films with \( 0 \leq x \leq 0.03 \) show superconductivity. When we annealed films at \( T_a = 300 \) °C, The superconducting transition temperature \( T_c \) lies between 0.5 K and 2.0 K. However, we do not see systematic change of \( T_c \). On the contrary, films annealed at \( T_a = 200 \) °C show the systematic change of \( T_c \); the value of \( T_c \) monotonically increases with increase of annealing time.

Figure 1(a) shows X-ray diffraction patterns for films with three different concentrations \( x \), \( x = 0.01, 0.03 \) and 0.05. We can recognize that all films are crystallized. Figure 1(b) shows the TEM cross sectional image for the IZO with \( x = 0.005 \). It is found that the film has a smooth surface and the film consists from grains with the size of 0.15-0.20 \( \mu \)m. We succeeded to observe the micro-structure in a small gain by the high resolution TEM for both films with \( x = 0.005 \) showing superconductivity and with \( x = 0.05 \) showing no superconductivity. From the Fast Fourier Transformations (FFT), it is found that there is a difference of structure between two films. It is known that IZO takes at least two different structures, bixbyite and rhombohedral phase [6]. From the fact that the superconducting film with \( x = 0.005 \) takes the metastable bixbyite, it seems that the appearance of superconductivity is strongly related to the film structure.

In Fig. 2(a), the resistive transition for different applied perpendicular magnetic fields to the film surface are shown for the film with \( x = 0.005 \). The inset shows the data measured at \( H = 0 \) T and \( H = 5 \) T in the relatively high temperature region. We observed large negative magneto-resistivity at normal state. The detailed discussion will be shown later. Figure 2(b) shows the temperature dependence of the upper critical magnetic field \( H_{c2} \). In the \( \rho - T \) curves at a constant applied magnetic field \( H \), \( T_c(H) \) was defined as a temperature at which half of the
normal state resistance was restored. Although the data show a positive curvature near $T_c$, we can obtain some properties from the linear approximation of $H_{c2}(T)$. According to Ginzburg-Landau theory, the coherent length $\xi(0)$ is given by $\xi(0) = \left\{\langle 0|\phi_0/2\pi T_c\rangle[(dH_d/dT)_T=T_c]\right\}^{-1/2} \equiv [(\phi_0/2\pi T_c)S]^{-1/2}$, where $\phi_0$ is the flux quantum ($\phi_0 = \hbar c/2e = 2.07 \times 10^{-15}$ Wb). Using the value of $S$ determined in Fig. 3 and the above relation, we obtain the length $\xi(0) \approx 10$ nm. From the formula $S = 4k_B/\pi eD$, where $D$ is the diffusion constant, using the free electron model, we can also obtain the relation for the coefficient of the electronic heat capacity as follows [7], $\gamma = 2.23 \times 10^{-4}\sigma_n S$, where $\sigma_n$ is the normal state conductivity. For the present film, $\gamma \approx 3.5$ has been obtained using values of $\sigma_n$ and $S$. This value is very small compared to that of pure In, $\gamma_{\text{In}} \approx 110$. This fact is consistent to the experimental result that the determined carrier density $n$ of this film is so small as $\approx 1.5 \times 10^{23}$ m$^{-3}$.

Next, we show the data of films with $x = 0.01$ annealed at $T_a = 200$ °C. Figure 3(a) shows the curves for different values of annealing time $t_a$, where the data on a-IZO ($t_a = 0$) film are also included. The resistivity increases with increasing $t_a$. Although the film annealed for $t_a = 20$ h shows the insulating property, other films show the metallic behavior at whole temperature region. As for superconductivity, all films except a-IZO show the superconducting transition. From the comparison of $\rho(H,T)$ characteristics between the film annealed at $T_a = 200$ °C and the film annealed at $T_a = 300$ °C shown in Figs. 3(a) and (b), it is found that although the value of $S$ is almost identical, the $T_c$ increases to 3.2 K from 2.0 K. Figure 3(b) shows $t_a$ dependence of $T_c$. It is clear that the $T_c$ changes systematically: The $T_c$ shows an initial sharp increase and changes slowly to saturate with $t_a$. On the contrary, the carrier density $n$ decreases sharply at initial stages and seems to saturate with increase of $t_a$. For instances, we obtained the values of $n$ as follows, $n(t_a = 0) = 4.8 \times 10^{26}$ m$^{-3}$, $n(t_a = 1$ h$) = 1.0 \times 10^{26}$ m$^{-3}$ and $n(t_a = 20$ h$) = 0.26 \times 10^{26}$ m$^{-3}$.

The $n$ dependence of $T_c$ cannot be explained by the BCS theory in which $T_c$ is given by $T_c = 1.13\Theta_D \exp[-(1/gN_F)]$, where $\Theta_D$, $g$ and $N_F$ are the Debye temperature, the coupling constant and the density of states at Fermi energy, respectively, if we assume that the value of $g$ is constant and the free electron model is valid. As mentioned above, there is a possibility that the change of the crystal structure brings superconductivity. Therefore, it is necessary to further study the crystal structure of each film annealed at different $t_a$ for further investigation.

Figure 2. Superconducting characteristics of the IZO film ($x = 0.005$) annealed at 300 °C for 2 h. (a) characteristics at a constant applied magnetic field. The inset shows the curves at normal state resistance was restored. Although the data show a positive curvature near $T_c$, we can obtain some properties from the linear approximation of $H_{c2}(T)$. According to Ginzburg-Landau theory, the coherent length $\xi(0)$ is given by $\xi(0) = \left\{\langle 0|\phi_0/2\pi T_c\rangle[(dH_d/dT)_T=T_c]\right\}^{-1/2} \equiv [(\phi_0/2\pi T_c)S]^{-1/2}$, where $\phi_0$ is the flux quantum ($\phi_0 = \hbar c/2e = 2.07 \times 10^{-15}$ Wb). Using the value of $S$ determined in Fig. 3 and the above relation, we obtain the length $\xi(0) \approx 10$ nm. From the formula $S = 4k_B/\pi eD$, where $D$ is the diffusion constant, using the free electron model, we can also obtain the relation for the coefficient of the electronic heat capacity as follows [7], $\gamma = 2.23 \times 10^{-4}\sigma_n S$, where $\sigma_n$ is the normal state conductivity. For the present film, $\gamma \approx 3.5$ has been obtained using values of $\sigma_n$ and $S$. This value is very small compared to that of pure In, $\gamma_{\text{In}} \approx 110$. This fact is consistent to the experimental result that the determined carrier density $n$ of this film is so small as $\approx 1.5 \times 10^{23}$ m$^{-3}$.

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Figure 3. Some characteristics of films with $x = 0.01$ annealed at 200 °C. (a)$T$ dependence of $\rho$ in $H$ = 0 T. Each mark shows data of films annealed for $t_a$ = 0, 0.5, 1.0, 2.0, 4.0 and 20 hours from bottom to top. The right and left vertical axes correspond to data of film with $t_a$ = 20 hours and the data of other films, respectively. (b)$t_a$ dependence of $T_c$.

of the superconductivity.

For the In$_2$O$_3$ film with $T_c(H = 0)$ ≈ 0.5 K annealed in N$_2$ gas at $T_a$ = 300 °C, we measured the magneto-resistivity $\Delta \rho$ defined by $\Delta \rho \equiv \rho(H) - \rho(0)$ at several temperatures above 1.5 K. When the magnetic field increases, the $\Delta \rho$ initially increases due to the destruction of superconductivity. As the field increases further, $\Delta \rho$ takes the maximum at a certain value $H_m$. Therefore, $\Delta \rho$ shows the negative differential value beyond $H_m$. At temperature and field regions below $T \approx 2$ K and below $H \approx 5$ T, $\Delta \rho$ takes positive values in spite of $d\Delta \rho/dH < 0$ at high fields. As increasing temperature, the value of $H_m$ decreases. At temperatures above 3 K, $\Delta \rho$ takes a negative value at higher magnetic fields. Finally, at temperatures higher than $T \approx 6$ K, $\Delta \rho$ takes the negative values at whole region. Whereas the positive $\Delta \rho$ at low fields and low temperatures mainly comes from the destruction of superconductivity by the magnetic field, the quantum correction due to the electron-electron interaction in dirty systems will give a dominant contribution to $\Delta \rho$ at larger magnetic field and at higher temperatures. In the case of the weak spin orbit scattering, the correction brings the negative $\Delta \rho$. Such negative $\Delta \rho$ in transparent oxide materials has been investigated in two and three dimensional a-IZO films [3]. Then, the present results of $\Delta \rho$ are explained by the competition of the destructions of superconductivity and localization (and/or electron-electron interaction) by magnetic fields.

In summary, we have shown the occurrence of superconductivity in crystalline IZO films annealed in air. From the HRTEM images, we confirmed that there is a difference of crystal structure between the superconducting and non-superconducting films. From the data of $H_{c2}(T)$, we estimated the values of coherence length and the coefficient of the electronic heat capacity.

References
[1] Minami T, Kasumu T and Takata S 1996 J. Vac. Technol. A 14 1704
[2] Jung Y S, Seo J Y, Lee D W and Jeon D Y 2003 Thin Solid Films 445 63
[3] Shinozaki B, Makise K, Shimane Y, Nakamura H and Inoue K 2007 J. Phys. Soc. Jpn. 76 074718
[4] Mori N 1993 J. Appl. Phys. 73 1327
[5] Sasabayashi T, Ito N, Nishimura E, Kon M, Song P K, Utumi K, Kajo A and Shigesato Y 2003 Thin Solid Films 445 219
[6] Yaglioglu B, Huang Y J, Yeom Y H and Paine D C 2006 Thin Solid Films 496 89
[7] Saint-James D, Sarma G and Thomas E J 1969 Type II superconductivity (International series of monographs in nature philosophy vol. 19) ed Ter Haar (Pegamon Press) p174