Characteristics of $T_c$ and $\rho(T)$ of polycrystalline (In$_2$O$_3$)-(ZnO) films with low carrier density

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Abstract. For the polycrystalline (In$_2$O$_3$)-(ZnO) prepared by annealing in air, we investigated the relation among superconductivity, $\rho(T)$ characteristics and preparation conditions. To clarify the distribution of elements, we studied the microstructure by scanning transmission electron microscopy (STEM) and electron energy-loss spectroscopy (EELS). It was found that 1) The films annealed at restricted regions of annealing temperature $T_a$ and time $t_a$ show the superconductivity. Transition temperature $T_c$ and carrier density $n$ are $T_c<$3.3K and $n \approx 10^{25}/m^3 \sim 10^{26}/m^3$, respectively. 2) The data on EELS spectra mapping of indium plasmon indicate that droplets of the pure indium phase distribute discretely on grain boundaries and near the interface between the film and the glass substrate. 3) Although data in the $T_c$-$T_a$ relation are scattered, the $T_c$ shows relatively good correlation with $n$, taking a convex form.

1. Introduction

Transparent electrode materials as In$_2$O$_3$ and tin-doped indium oxide (ITO) have been already used in application as devices. Amorphous indium zinc oxide (a-In$_2$O$_3$-ZnO) films have practically attracted considerable interest because of a smooth surface and large Hall mobility $\mu$. [1]

Regarding a-(In$_2$O$_3$)-(ZnO) films of which weight concentration $x$ of ZnO is about 0.1, we have examined the electrical properties at temperatures 2.0K$<T<$300K. [2,3] Temperature dependence of the resistivity $\rho$ of films with thickness $d=350$nm show the metallic characteristics, that is $dp/dT > 0$, in a wide temperature region. On the other hand, annealing in air induces large change of $\rho$ and $n$, because the free carriers are supplied by oxygen deficiency as well as substitutional Zn. However, we did not observe the superconductivity. As for an appearance of superconductivity, Mori

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found that the ITO films annealed under proper conditions show the sharp superconducting transition.\cite{4} Regarding In$_x$O films, Kowal and Ovadyahu \cite{5} showed that films with $n$ smaller than \( \approx 10^{26} / m^3 \) do not show the superconductivity. Occurrence of superconductivity in low carrier materials is one of most fundamental topics in solid state physics at low temperatures.

As shown in previous report \cite{2}, we have investigated the effects of crystallinity on $T_c$ for (In$_2$O$_3$)$_{1-x}$(ZnO)$_x$ films with $x=0.01$. These films show the systematic changes of $T_c$ with increase of XRD diffraction intensity. In this work, for (In$_2$O$_3$)$_{1-x}$(ZnO)$_x$ films with various $x$ between $0 \leq x \leq 0.035$ prepared by different annealing conditions, we report superconductivity from the view point of the relation between $T_c$ and carrier density $n$. We also investigated the crystallinity by XRD analyses and the film structure by the high resolution transmission electron microscopy (HRTEM). Further, we use electron energy-loss spectroscopy in a TEM (TEM-EELS) to find the relation between the transport characteristics and micro- and nano-structure of the present materials.

2. Experimental detail

We measured the temperature dependence of $\rho$ and Hall coefficient $R_{HH}$, using a standard dc four-probe technique. Regarding the measurement of $R_{HH}$, we applied a magnetic field of $H=\pm 5$ T perpendicular to the film surface. Properties of $\rho$, $n$ and mobility $\mu$ were measured in a range from 0.5K to 300 K. The detailed procedure has been given in the previous work. \cite{6}

3. Results and discussion

Regarding the film with $x=0.01$ annealed at annealing temperature $T_a=200^\circ$C for annealing time $t_a=20h$, Figs. 1(a) shows $R(T)$ curves. Figure 1(b) shows the red-green-black (RGB) image of a map of indium plasmon obtained by STEM EELS spectra mapping. We can see some distinct regions marked by red. From the plasmon distribution spectra obtained by EELS spectra, we confirmed that low-loss EELS spectra taken in the regions marked by red correspond to the bulk plasmon peak for pure indium. Although the spectra indicate the existence of pure indium droplets, these droplets discontinuously appear and the size is a few nanometers. Therefore, we consider that the superconductivity cannot be assigned to continuous metallic indium channels.\cite{7} Detail analysis is shown in the previous work.\cite{2,3}

Now, we will show experimental results in contrast with the previous one.\cite{2} Figure 2 shows the $t_a$ dependence of $T_c$ for films with $x=0.01$ annealed at $T_a=300^\circ$C. The inset shows the X-ray diffraction (XRD) patterns for different $t_a$. We cannot find any relation between superconductivity and crystallinity. When we take into account of the present result, we must conclude that the value of $T_c$ cannot be determined by only the crystallinity.

Figure 3 shows $T_a$ dependence of $T_c$ for films with $x=0.025$ annealed at three different $t_a=0.5h$, 1 h and 4h. For all cases of $t_a$, it is found that the $T_c$ decreases with increase of $T_a$. This means that $T_c$ does not be determined by $T_a$, namely, crystallinity. On the other hand, as shown in the inset, it seems that the $T_c$ has a good correlation with carrier density $n$. With regard to the film with $x=0.025$, superconductivity seems to be restricted in the convex region in the $T_c - n$ relation.
Figure 1. (a) $R-T$ curves at different magnetic fields for film with $x = 0.01$ annealed at $T_a = 200\,^\circ C$ for 2h. (b) Map of indium plasmon intensity obtained by MLLS fitting. Red marks correspond to the pure indium regions.

Figure 2. $t_a$ dependence of $T_c$ for films with $x = 0.01$ annealed at $T_a = 300\,^\circ C$. Inset shows XRD patterns of films for $t_a = 0.25, 0.5, 1, 2, 4$ and $20h$ from bottom to top.

Figure 3. $T_a$ dependence of $T_c$ for films with $x = 0.025$ for different $t_a$. The inset shows the $n$ dependence of $T_c$.

Figure 4. $n$ dependence of $T_c$ for all films with different $x$ prepared by various conditions.

To complete the $n$ dependence of $T_c$, in Figure 4, we summarize the data of films with several values of $x$ annealed under the various conditions. Regarding the $n$, superconductivity appears in the region $0.1 \times 10^{26} / m^3 < n < 3 \times 10^{26} / m^3$. As shown by solid and broken lines, the boundary between superconducting and non-superconducting phases takes a convex taking a maximum approximately around $n^* \approx (0.5 - 0.6) \times 10^{26} / m^3$. The non-superconducting phase is divided into insulating (I) and metallic (M) phases by dotted line near $n = n^*$. In I and M phases, $\rho(T)$ shows the characteristics of $d\rho/dT < 0$ and $d\rho/dT > 0$, respectively. These different characteristics can be seen in the S phase: The open marks in the low $n$ region show $T_c$ of films showing $d\rho/dT < 0$ at temperatures above $T_c$. On the contrary, the closed marks show $T_c$ of films showing the $d\rho/dT > 0$ above $T_c$. Taking
account of the relation between \( n \) and \( \rho \), we can obtain almost the same convex relation between \( T_c \) and \( \rho \) as that in Fig.4; the superconducting phase appears in the region of \( 4 \times 10^{-6} \Omega m < \rho < 5 \times 10^{-4} \Omega m \). In the \( T_c - \rho \) diagram, superconducting films in the lower \( \rho \) region below \( \rho \approx 4 \times 10^{-5} \Omega m \) show the metallic behavior above \( T_c \). It is General that when the \( n \) decreases and/or \( \rho \) increases, the electron localization will be dominant at low temperatures to depress the superconducting transition temperature. However, the present oxide films shows the opposite dependence in the higher region of \( n \); \( T_c \) increases with decrease of \( n \). Such behavior that \( T_c \) increases with increase of localization is reported for the system of boron doped diamond. In this case, an idea that effective attraction interaction increases with increase of localization is suggested. [8] For the exact reason of appearance of superconductivity shown in Fig.5, it is necessary further theoretical and experimental investigations.

4. Conclusions

In conclusion, we have investigated the microstructure and the transport properties, regarding polycrystalline \((\text{In}_2\text{O}_3)_{1-x}(\text{ZnO})_x\) films annealed in air. From the detailed analysis of EELS observation, the distribution of indium droplets was found to be scattered. We consider that the superconductivity in the present indium zinc oxide films cannot be assigned to continuous metallic indium channels. From the investigations for many films with different concentration of ZnO prepared by various annealing conditions, we obtained phase diagram between \( T_c \) and \( n \). We found that the superconducting phase is restricted \( n \) region inside a convex curve.

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