Microscopic structure and electrical transport property of sputter-deposited amorphous indium-gallium-zinc oxide semiconductor films

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Abstract. We report on microscopic structures and electrical and optical properties of sputter-deposited amorphous indium-gallium-zinc oxide (a-IGZO) films. From electron microscopy observations and an x-ray small angle scattering analysis, it has been confirmed that the sputtered a-IGZO films consist of a columnar structure. However, krypton gas adsorption measurement revealed that boundaries of the columnar grains are not open-pores. The conductivity of the sputter-deposited a-IGZO films shows a change as large as seven orders of magnitude depending on post-annealing atmosphere; it is increased by N₂-annealing and decreased by O₂-annealing reversibly, at a temperature as low as 300°C. This large variation in conductivity is attributed to thermionic emission of carrier electrons through potential barriers at the grain boundaries, because temperature dependences of the carrier density and the Hall mobility exhibit thermal activation behaviours. The optical band-gap energy of the a-IGZO films changes between before and after annealing, but is independent of the annealing atmosphere, in contrast to the noticeable dependence of conductivity described above. For exploring other possibilities of a-IGZO, we formed multilayer films with an artificial periodic lattice structure consisting of amorphous InO, GaO, and ZnO layers, as an imitation of the layer-structured InGaZnO₄ homologous phase. The hall mobility of the multilayer films was almost constant for thicknesses of the constituent layer between 1 and 6 Ǻ, suggesting rather small contribution of lateral two-dimensional conduction. It increased with increasing the thickness in the range from 6 to 15 Ǻ, perhaps owing to an enhancement of two-dimensional conduction in InO layers.

1. Introduction

Amorphous In-Ga-Zn-O (a-IGZO) films have attracted much attention since the first report on a thin-film transistors (TFTs) with an a-IGZO channel [1] and a subsequent report on a TFT using a sputter-deposited a-IGZO thin film [2]. As a result, many researchers have improved characteristics of a-IGZO TFTs and consequently demonstrate a high field-effect mobility of about 10 cm²V⁻¹s⁻¹, a small subthreshold swing down to 0.063 Vdec⁻¹ [3], a large on-off current ratio greater than 10¹⁰ with a very low off-current lower than 10⁻¹⁴ A [4], excellent short-range uniformity [5], and high frequency operation in ring oscillator circuits [6]. Lately, a lot of electronics companies have launched research and development on amorphous oxide semiconductors and their application to TFTs using them as
channel materials, in order to replace amorphous silicon (a-Si) TFTs and low temperature polycrystalline silicon (LTPS) TFTs, which have limitations inhibiting realization of future flat panel displays (e.g., low carrier mobility of a-Si and difficulty in large area formation of LTPS). The companies have eagerly demonstrated prototype electronic devices using a-IGZO TFTs as switching and driving elements for flat-panel displays, including organic light-emitting diode (OLED) displays, liquid crystal displays (LEDs), and flexible displays, which exhibit attractive features such as a high speed, high resolution, and low power-consumption. Nowadays, at an exhibition of home-electronics or a conference on displays, we can witness prototypes of attractive displays which are announced to be released in the near future, such as high-resolution (4k2k) large-sized (over 50 inches) OLED/LCD TVs and full-colour flexible OLED displays using a-IGZO TFTs. More recently, attempts to apply amorphous oxide semiconductors also to other electronic devices have been started; e.g. combining sputter-deposited n-type IGZO TFT technology with sputter-deposited p-type tin oxide TFT technology [7] and exploiting their characters of low-temperature manufacturing, a high-voltage complementary inverter on Si-LSI Cu-interconnects with n-type IGZO and p-type SnO channels has recently been demonstrated [8].

As mentioned above, research on a-IGZO TFTs and their application to electronic devices have been eagerly conducted, but fundamental properties of a-IGZO films have not been so much reported, comparably. For further development of a-IGZO TFTs and their application, it should be important to understand the mechanism of electron conduction in a-IGZO, that is, the reason why this material has larger electron mobility than other amorphous semiconductors. In order to obtain information on the conduction mechanism, dependence of electric properties on thermal treatment conditions should be investigated, because thermal treatment can change the electric conduction properties, as deposition conditions such as sputtering gas composition do [2]. Understanding the effect of post-deposition thermal treatment is also important, in view of fabrication process optimization, because a-IGZO films should experience a lot of thermal processes in a flow of manufacturing a device incorporating them. Here, we present our experimental results on microscopic structures, electrical transport properties and optical properties of sputter deposited a-IGZO films having received post-deposition annealing, which would give a clear prospect of obtaining an insight into the mechanism of electric conduction in a-IGZO.

Further, we introduce an additional topic of a-IGZO: a multilayer artificial lattice fabricated by depositing constituent layers of amorphous InOₓ, GaOₓ and ZnOₓ to imitate the two-dimensional layered structure of crystalline InGaZnO₄. Although investigation on artificial lattice films with layers of a conventional amorphous semiconductor material such as a-Si was reported a lot [9,10], there are only a few reports on artificial lattice films consisting of amorphous oxide semiconductor layers. This study on such an artificial lattice was carried out as a challenge of expanding possibility of amorphous oxide semiconductors.

2. Experimental details
The a-IGZO films were deposited on 20 × 20 mm² or 3 inch-diameter substrates by radio frequency (rf) magnetron sputtering using a polycrystalline InGaZnO₄ (or other compositions as needed) ceramic target of 3 inch in diameter (Toshima manufacturing Ltd.) in mixed gases of Ar and O₂. We employed two types of sputtering geometries in terms of the substrate to target positional relationship, that is, an off-axis (diagonal) one and an on-axis (face-to-face) one. Films prepared by the on-axis geometry deposition were used in room-temperature Hall effect measurements on 30 nm- and 300 nm-thick films and for optical measurements. Films prepared by the off-axis geometry deposition was used in the other experiments. In the off-axis geometry, a 3-inch diameter substrate holder was positioned to be diagonally opposite to the sputtering target with an off-axis angle of about 35 degrees, where the surface of a substrate placed on the holder was parallel to the target surface and the distance between the target-centre and the substrate-holder-centre was 130 mm. In the on-axis geometry, a substrate was placed in front of the target to face it at a distance of 125 mm. Standard deposition conditions were as follows: an input rf power of 200 W, a sputtering gas pressure of 0.50 Pa, no intentional substrate
heating for the both sputtering geometries, and \( \text{O}_2/(\text{Ar}+\text{O}_2) \) molar ratio of 5 and 1 mol% for the off-axis geometry and the on-axis geometry, respectively. It has been confirmed that there was no significant difference in electrical properties (conductivity, mobility, etc.) between the a-IGZO films prepared by the off-axis geometry deposition and those by the on-axis geometry deposition when deposited under the standard conditions.

Film compositions were analyzed using an x-ray fluorescence (XRF) apparatus (Rigaku ZSX 100e). In-\text{L}\alpha, Ga-\text{K}\alpha and Zn-\text{K}\alpha emissions exited by x-ray from a rhodium tube were detected, and In:Ga:Zn composition ratios were calculated by the fundamental parameter method. Typical composition ratios of a-IGZO films deposited with the off-axis geometry and the on-axis geometry were In:Ga:Zn of 1:0.9:0.6 and 1:1.1:0.8, respectively. We already confirmed before that the electrical properties of a-IGZO are hardly affected by this extent of fluctuation in composition around the nominal composition 1:1:1, in particular in Zn content [2]. For basic characterization, x-ray diffraction (XRD) and x-ray reflectivity (XRR) were carried out using a parallel beam x-ray diffractometer (Philips X'pert MRD) with a multilayer x-ray mirror and a copper tube. A typical value of the mass density of the sputter-deposited a-IGZO films evaluated by XRR was approximately 6.0 g cm\(^{-3}\).

The deposited films were annealed in a tube-furnace with a fused-silica core-tube (1400 mm in length, 150 mm in diameter) under an \( \text{N}_2 \) or \( \text{O}_2 \) gas flow of a few litres per minute. The standard time duration of the annealing in \( \text{N}_2 \) (\( \text{N}_2\)-annealing) or \( \text{O}_2 \) (\( \text{O}_2\)-annealing) was 1 hour for 30 nm- and 40 nm-thick films, and 10 hours for 300 nm-thick films. Both the \( \text{N}_2\)- and \( \text{O}_2\)-annealings were applied to some films in a sequential combination (hereafter, referred to as \( \text{N}_2\)-annealing+\( \text{O}_2\)-annealing\)). A sealed-vessel-type tube-furnace was used for \( \text{H}_2 \) annealing treatment in a mixture of 2\% \( \text{H}_2 \) and 98\% \( \text{He} \) gases after gas-exchange by evacuating and flushing. Some of the a-IGZO films were crystallized by high-temperature annealing at above 700\°C in air in a box furnace with molybdenum silicide heaters.

Most of the a-IGZO films used for electrical measurements were deposited on a thermally-grown \( \text{SiO}_2 \) (100 nm in thickness) layer over a Si substrate or on a glass (Corning #1737) substrate. Highly conductive a-IGZO films were formed on a Si substrate coated with a silicon nitride (Si\( \text{N}_x \)) layer deposited by plasma-enhanced chemical vapour deposition (PECVD), using an effective diffusion of hydrogen from the PECVD-Si\( \text{N}_x \) layer into the a-IGZO film.

Cross-sectional micro-structures of the a-IGZO films were observed by transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM) using a Tecnai F30 (FEI Co.) operating at 300 keV. The TEM specimens were prepared by focused ion-beam (FIB) irradiation followed by low-energy argon ion-milling (1 keV and 300 eV) using a Gentle Mill (Technoorg Linda Ltd. Co.) to remove a damage layer created by the FIB irradiation. Bright-field images were acquired under significantly underfocused conditions to emphasize the Fresnel contrast of grain boundaries in the films. Plan-view images of the film surfaces were observed by scanning electron microscopy (SEM) using an S-5500 (Hitachi High-Technologies Corp.) operating at 30 kV.

Grazing incidence small-angle x-ray scattering (GISAXS) was carried out at the BL46XU beamline of SPring-8. Incident x-rays were monochromatized to 12 keV and set at an angle of 0.15° with respect to the film surface, which was slightly lower than the critical angle of total reflection for the a-IGZO films. Scattered x-ray beams were detected using a scintillation counter scanned in an in-plane angle (2\( \theta \)) range from 0.05° to 3.50°. The specimens were held in a helium gas chamber to reduce a background signal generated by air-scattering.

To investigate the local coordination structure in the a-IGZO films, In, Ga, and Zn K-edge x-ray absorption fine structure (XAFS) spectra were collected at the BL19B2 beamline of SPring-8. We employed a transmission geometry using specimens of a-IGZO films removed from the substrates and then mixed with boron nitride powders in order to obtain more accurate information than that by the fluorescence method, because a background signal can be readily subtracted from thus obtained XAFS spectra. Polycrystalline InGaZnO\(_4\) powders were also measured as a reference.

In order to investigate mesoscopic film structures, the effective surface area was estimated by gas-adsorption surface-area analysis based on the Brunauer-Emmett-Teller (BET) method using krypton (Kr) gas. A sample of a-IGZO film on a thin Si substrate (100 \( \mu \)m in thickness) whose surfaces are
both mirror-polished and covered with a thermal SiO$_2$ layer was cut into small chips and then packed in a sample cell as dense as possible. Each sample cell thus containing approximately 2.5 g of a-IGZO-coated Si substrate chips packed in the cell was baked at 300°C for about 50 hours in vacuum, before introducing Kr gas into the cell at 77 K. Two sets of measurements using different cells were executed for each sample on a-IGZO film to confirm the reproducibility.

The electrical conductivity and the Hall coefficient were measured at room temperature by the van der Pauw method using a Hall effect measurement system (Accent HL5500PC) with a high-resistivity buffer amplifier. The applied voltage between the electrodes was 20 mV and the magnetic field was 0.5 Tesla. Temperature dependences of the electrical conductivity, Hall effect, and magneto-resistance were measured using a physical property measurement system (PPMS, Quantum Design) with a semiconductor characterization system (Keithley 4200-SCS) in a temperature range from 2 to 370 K. The magnetic field for the Hall measurement was 1 Tesla. The magnetic field was swept up to 9 Tesla in the magneto-resistance measurement. For these electrical measurements, stacked electrodes of a 100 nm-thick gold layer on a 5 nm-thick titanium layer were formed on the a-IGZO films by electron-beam evaporation or sputtering thorough a metallic shadow mask.

If either of n- and p-type carriers is dominant in electrical conduction, the carrier density $N$ can be calculated from the Hall coefficient, $R_H = r_H q_c N$, where $q_c$ is the elementary charge of a carrier and $r_H$ is the Hall factor which is equivalent to unity for degenerate semiconductors and slightly deviates from unity for non-degenerate semiconductors, depending on the carrier energy (type of scattering) [11]. We assume that there is no contribution of holes to electrical conduction in a-IGZO and $r_H = 1$ can be used even for non-degenerate semiconductor a-IGZO films.

To evaluate the optical coefficients of a-IGZO, optical transmission and reflection spectra were measured on a-IGZO films on fused-silica substrate at a wavelength range of 240-2400 nm covering ultraviolet (UV), visible (VIS) and near-infrared (NIR) regions, using a Hitachi U-4100 spectrometer. The optical absorption coefficient, $\alpha$, was determined by $T_r = \exp(-\alpha d)$, where $T_r$ is the transmittance and $d$ is the film thickness. The transmittance was corrected as $T_r = T_m/(1-R_m)$, where $T_m$ and $R_m$ are the measured transmittance and reflectance of the films, respectively, to eliminate the interface-interference effect which is often observed as fringes in the $T_m$ and $R_m$ spectra in transparent regions [12].

Spectroscopic ellipsometry measurement was carried out on a-IGZO films on heavily-doped silicon substrate coated with a thermal SiO$_2$ layer (100 nm in thickness), using an ellipsometer with a rotating-compensator instrument (M-2000, J. A. Woollam Co., Inc.) at wavelengths ranging 190-1690 nm. The measured spectra were analysed by minimum mean-square fitting with appropriate optical models.

For fabricating amorphous multilayer thin films, constituent layers of amorphous InO, GaO, ZnO and MgO were deposited at room temperature by pulsed laser deposition (PLD) using a computer-controlled PLD system (Pascal Co. Ltd.). A KrF excimer laser source (Lambda physik) with a wavelength of 248 nm and laser pulse duration of 25 ns was employed as a light source of the PLD. The laser pulse energy and repetition frequency were 50 mJ and 2 Hz, respectively, and focused spot size of the laser onto a target was controlled to 1 mm$^2$ or less. Commercially available In$_2$O$_3$, Ga$_2$O$_3$, ZnO and MgO ceramic pellets were employed as the targets. The deposition atmosphere was pure oxygen kept at 1 Pa. Constituent layers were stacked one by one, using the computer-controlled PLD system, where the thickness of each constituent layer was automatically controlled to be an intended value by irradiating a corresponding number of laser pulses determined in advance.

3. Results

3.1. Microscopic structural analyses

3.1.1. Electron microscopy
A cross-sectional TEM image of an 100 nm-thick a-IGZO film on a Si substrate is shown in figure 1. The film looks uniform with no microstructure in the lower region extending from the a-IGZO/Si
interface to 30 nm above it. In contrast, in the upper region, a number of bright lines are seen running perpendicularly to the film surface, which can be regarded as boundaries of a columnar structure with a column width of 20 nm. No electron-diffraction spot was observed with a plan-view TEM geometry, which implies that this IGZO film is in an amorphous state even though it has the columnar structure in the upper region. This columnar-structure in the a-IGZO films on Si was clearly observed also by cross-sectional scanning transmission electron microscopy (STEM), as shown in figure 2(a). Simultaneously, electron diffraction data obtained with a nm-size electron beam in the STEM system revealed that this IGZO film is wholly amorphous. As can be seen in figure 2(b), an a-IGZO film on SiO2 shows an amorphous columnar structure, similar to that on Si.

![Figure 1](image)

**Figure 1.** Bright-field cross-sectional TEM image of a 100 nm-thick a-IGZO film on Si substrate. Carbon and Cr films were deposited on the a-IGZO film to protect and define the surface of the a-IGZO film.

Formation of the columnar structure observed in the upper region of the films is probably related to the film deposition conditions. It is known that sputter-deposited films show a variety of microstructures depending on sputtering-gas pressure, substrate temperature, input power, and so on [13]. It was reported that amorphous silicon films deposited by sputtering, for example, showed a columnar microstructure when deposited under a certain deposition condition, and other structures (uniform, granular, etc.) under different conditions [14]. Referring to these previous studies, it is considered that the deposition conditions employed in this study led to the formation of the uniform structure near the film/substrate interface and the micro-columnar structure in the upper region of the films.

Surface plan-view SEM images of 20 nm-, 40 nm-, and 100 nm-thick a-IGZO films are shown in figures 3(a), (b), and (c), respectively. The contrast seen in these images originates in not only the surface roughness but also inhomogeneity of mass density in the films, since the SEM apparatus employed in this study possesses a higher sensitivity to mass density than conventional SEM apparatuses because of the special geometrical alignment of the electron detector placed in front of the specimen. The surfaces of the a-IGZO films having thicknesses of 40 nm [figure 3(b)] and 100 nm [figure 3(c)] show granular-like-structures with grain sizes of about 20 and 30 nm, respectively, which are comparable to the column width observed in the cross-sectional TEM/STEM images [figures 1 and 2]. Also in the surface SEM image of the 20 nm-thick a-IGZO film [figure 3(a)], which exhibits a lower contrast than the others, we can see a similar granular-like structure on the surface. Although the 20 nm-thick region near the film/substrate interface looks uniform in the cross-sectional TEM/STEM images [figures 1 and 2], a columnar structure could exist even in the 20 nm-thick film as well as the thicker films. The diameter of the columns in the 20 nm-thick film is about 15 nm, which is slightly smaller than that of the 100 nm-thick films (~30 nm) and of the 40 nm-thick films (~20 nm). The grain size seems to increase with increasing film thickness.
3.1.2. In-plane GISAXS
Figure 4 shows in-plane GISAXS profiles of 20 nm-thick a-IGZO films deposited on (a) SiO$_2$/Si and (b) Si substrates. In the figures, GISAXS profiles of the respective substrates without an a-IGZO films are also shown as references. As can be seen there, the GISAXS profile of the a-IGZO films on SiO$_2$ has an obvious peak at a scattering vector value, $Q \approx 0.04$ Å$^{-1}$, and the scattering profile of the a-IGZO films on Si shows significant scattering intensity in the similar range of $Q$. These GISAXS profiles suggest a lateral correlation between grains in the a-IGZO films with an average in-plane distance of 10 nm between the centres of neighbouring grains. This result is consistent with that obtained from the plan-view SEM image of a 20 nm-thick a-IGZO film [figure 3(a)], which gave an average column width of 15 nm.

It is also found in comparison between the GISAXS profiles of a-IGZO on SiO$_2$/Si and Si that distribution of the grain distance is dependent on the substrate. The peak of a-IGZO on the Si substrate is broader than on the SiO$_2$/Si substrate, indicating broader distribution of the grain distance.

3.1.3. X-ray diffraction for high-temperature-annealed IGZO films
The GISAXS results suggest that the sputter-deposited a-IGZO films each contain nano-regions whose density is different from the neighbours. A probable constitution is that with high density grains each surrounded by low density grain-boundaries, which is suggested by the TEM/STEM and SEM observations [figures 1, 2 and 3]. Another possibility is a compositional phase separation into In$_2$Ga$_2$ZnO$_7$-like and In$_2$Ga$_2$ZnO$_7$-like amorphous phases, because as described in Section 2, the films have a composition of In:Ga:Zn $\approx$ 1:0.9:0.6, which is between InGaZnO$_4$ (In:Ga:Zn = 1:1:1) and In$_2$Ga$_2$ZnO$_7$ (1:1:0.5), and there is no solid solution between InGaZnO$_4$ and In$_2$Ga$_2$ZnO$_7$ in the
crystalline In-Ga-Zn-O system. In order to confirm whether the compositional phase separation took place or not, transient states of the films from amorphous to crystalline ones were checked by means of x-ray diffraction.

![Figure 4](image1.png)  
**Figure 4.** GISAXS profiles of 20 nm-thick a-IGZO films on (a) SiO$_2$/Si and (b) Si substrates. GISAXS profiles of the substrates only are also shown with solid lines.

![Figure 5](image2.png)  
**Figure 5.** X-ray diffraction patterns of polycrystalline InGa$_{0.9}$Zn$_{0.6}$O$_x$ films on SiO$_2$/Si deposited at room temperature and annealed in air at (T$_{an}$ =) 700, 900 and 1100°C. The diffraction patterns were measured by $\omega$-2$\theta$ scan method. Arrows and inverse triangles indicate peaks of InGaZnO$_4$ and In$_2$Ga$_2$ZnO$_7$, respectively, with diffraction indices. For the 1100°C-annealed film, the peak at 34$^\circ$ is absent because the c-axis of In$_2$Ga$_2$ZnO$_7$ crystallites in the film are oriented normal to the substrate surface.

Figure 5 shows the x-ray diffraction patterns of IGZO films crystallized by post-deposition annealing in air at 700, 900 and 1100°C. The IGZO film annealed at 1100°C showed the phase separation into InGaZnO$_4$ and In$_2$Ga$_2$ZnO$_7$. According to the rocking curve ($\omega$-scan) measurement, the InGaZnO$_4$ phase was c-axis oriented, while In$_2$Ga$_2$ZnO$_7$ phase was randomly oriented. On the other hand, the IGZO films annealed at 700°C and 900°C showed broad diffraction peaks at angles between the diffraction peaks of InGaZnO$_4$ and In$_2$Ga$_2$ZnO$_7$. The peak around 31° for the 900°C annealed film indicated the onset of the phase separation. We suppose that the broad peaks for the 700°C-annealed IGZO film come from an intermediate phase between InGaZnO$_4$ and In$_2$Ga$_2$ZnO$_7$, which is probably a non-equilibrium phase having a layered structure similar to InGaZnO$_4$ or In$_2$Ga$_2$ZnO$_7$ with stacking faults, thus showing a lattice constant between those of InGaZnO$_4$ and In$_2$Ga$_2$ZnO$_7$. Since a temperature higher than 900°C is necessary to complete the phase separation into InGaZnO$_4$ and In$_2$Ga$_2$ZnO$_7$ phases, the GISAXS results are not due to such a kind of phase separation in the a-IGZO films with an intermediate composition.

3.1.4. Kr gas adsorption surface area analysis

O$_2$ or N$_2$ atmosphere affects the conductivity of a-IGZO films when they undergo annealing at a low temperature of 300°C or below, as will be described later. It was already reported that the carrier density of a-IGZO films and their TFT characteristics significantly change when exposed to an O$_2$ atmosphere [15]. Some polycrystalline oxide-semiconductor films used for gas sensors, such as SnO$_2$ films, change their conductivity by adsorbing gas molecules at the grain boundaries in the films [16,17], and accordingly the sidewall surface area of grains in such films can be evaluated by the Kr gas adsorption technique [18]. If the column (or grain) boundaries of a-IGZO films observed in the
cross-sectional TEM/STEM images (figures 1 and 2) were fine pores piercing the film from the surface, gas molecules could easily penetrate the films through the pores and react to form or dissipate potential barriers at the boundaries, thus resulting in wide variation of conductivity, as observed on polycrystalline oxide-semiconductor gas-sensor films and in hydrogen passivation of grain boundaries in polycrystalline Si films. The gas penetration and reaction should be enhanced by thermal treatment.

To investigate whether the column boundaries are such pores or not, Kr-gas-adsorption surface-area analysis was carried out on 40 nm- and 400 nm-thick a-IGZO films. The results are summarized in table 1. No inner-surface area is detectable for the 40 nm-thick a-IGZO film, since the measured surface area of the film is exactly the same as its planar dimension. On the other hand, the measured surface area of the 400 nm-thick a-IGZO film is about 50% larger than its planar dimension. According to the following analysis, this difference between the surface area and the planar dimension is probably due to the surface roughness of the 400 nm-thick film, and there should exist no such pores at the column boundaries.

| Table 1. Surface areas of a-IGZO films of 40 and 400 nm in thickness, estimated by Kr-gas-adsorption surface-area analysis with the BET method. Planar dimensions of the samples are also shown. |
|---------------------------------|-----------------|-----------------|
| surface area of film (m²)*   | planar dimension (m²) |
| 40 nm-thick a-IGZO film | 0.011          | 0.011          |
| 400 nm-thick a-IGZO film | 0.016          | 0.011          |

*Surface area of film was derived by subtracting the surface area of the sample cell from the measured gross surface area and then subtracting the area of back surface of SiO₂/Si substrate equal to the planar dimension of sample.

From the cross-sectional TEM image shown in figure 1, the surface roughness of the 100 nm-thick a-IGZO film is estimated to be 2-3 nm. The surface roughness could increase to 10 nm in the 400 nm-thick a-IGZO film, because the surface roughness usually increases monotonously with increasing film thickness. Assuming a simplified geometrical model for surface roughness estimation in which pyramids of 10 nm-height with a 20 × 20 nm² basal plane are laterally aligned, its total surface area is estimated to be approximately 1.4 times as large as its planar dimension. On the other hand, for the case where cylinders of 20 nm diameter are arranged into a square lattice, the total surface area of the columns' sidewalls should be much larger than the planar dimension (about 60 times as large as the planar dimension). Therefore, the adsorption on the inner-surfaces of the columns is not likely to be the cause of the observed difference of only 50%. Thus, the 50% increase of the measured surface area compared to the planar dimension should be explained as the effect of the surface roughness. We conclude, therefore, that the column boundaries observed in the cross-sectional TEM images are not pores through which gas molecules easily penetrate into the film. Variation in the conductivity of the a-IGZO films shown later in figure 6 is not attributed to the same mechanism as that dominating in the polycrystalline oxide semiconductor films used for O₂-gas sensors, such as SnO₂.

3.1.5 XAFS

In radial structural functions (RSFs) of a-IGZO films obtained from their XAFS spectra of In-K, Ga-K and Zn-K edges, obvious peaks of the nearest-neighbour M-O (M = In, Ga or Zn) pairs were observed, but no peak of the next-nearest-neighbour M-M pairs appeared, while both kinds of peaks were clearly seen in RSFs of crystalline InGaZnO₄ powders. These results confirm that the a-IGZO films have a disordered atomic arrangement unlike the crystalline IGZO.

The coordination numbers, each indicating the number of nearest-neighbour oxygen atoms around a metal atom, and the distance between nearest-neighbour M and O were estimated from each of the RSFs. Table 2 collects the first-shell fitting results on a sputter-deposited 20 nm-thick a-IGZO film using the ideal values calculated from the structural data on crystalline InGaZnO₄ [19]. Almost the
same results as the above were obtained for 100 nm-thick a-IGZO films formed with various conditions (e.g., no annealing or 300°C-annealing after room temperature deposition, and no annealing after 240°C-deposition). Radial distribution functions of 20 nm- and 100 nm-thick a-IGZO films formed with the same conditions as the above were also estimated by the grazing incident x-ray scattering and conventional x-ray scattering, using film-samples removed from the substrates. The results with respect to short-range inter-atomic distances are consistent with the RSFs obtained by the XAFS measurement.

Table 2. First shell fitting results on In-K, Ga-K and Zn-K edges EXAFS spectra of a sputter-deposited 20 nm-thick a-IGZO film and of commercial crystalline InGaZnO4 powders, along with the ideal values of crystalline InGaZnO4. CN is the coordination number of nearest-neighbour oxygen atoms around In, Ga or Zn, and r is the distance between the nearest-neighbour oxygen atoms and In, Ga or Zn..

|        | a-IGZO CN | crystalline InGaZnO4 CN | ideal* CN |          |
|--------|-----------|------------------------|-----------|---------|
| In-O   | 4.6       | 6.0                    | 6         | 2.14    |
| Ga-O   | 4.3       | 4.5                    | (Ga,Zn)-O | 1.93    |
| Zn-O   | 4.3       | 4.1                    | 1         | 2.01    |

* Calculated from the crystal structure data of an InGaZnO4 single crystal. Ga and Zn occupy the same site randomly, and this (Ga, Zn) site is coordinated by five oxygen atoms [19].

It should be noted that the coordination number (CN) of In-O in the a-IGZO films is remarkably smaller than that of the crystalline InGaZnO4, differently from the result reported by Cho et al [20]. Furthermore, the difference in the inter-atomic distance (r) of In-O between the a-IGZO film and the crystalline IGZO is comparably larger than those of Ga-O and Zn-O. These suggests that InO6 octahedrons in the a-IGZO film have an imperfect structure with a considerable number of oxygen vacancies.

3.2. Electrical transport properties

3.2.1. Conductivity variation with annealing conditions

The electrical conductivity of a-IGZO films is known to be able to be controlled by some deposition conditions such as the O2 partial pressure in sputtering atmosphere [2] and the substrate temperature. It is noteworthy that the conductivity of a-IGZO films widely change when annealed after their deposition and can be controlled by conditions of the annealing temperature and atmosphere. Figures 6(a) and (b) show annealing temperature dependences of the carrier density (N) and those of the conductivity (σ), respectively. When the films were annealed in N2 ambient, the carrier density drastically increased with increasing the annealing temperature up to nearly 300°C [closed circles in both figures 6(a) and (b)]. For example, an increase in the carrier density of five orders of magnitude was observed after N2-annealing at 300°C on 30 nm-thick a-IGZO films on glass, and that of nearly seven orders of magnitude was observed on the 40 nm-thick a-IGZO/SiO2/Si samples [open circles in figure 6(b)]. By contrast, the carrier density kept as low as 1013 cm-3 after annealing at 300°C in an O2 ambient [open triangle in figure 6(a)]. Furthermore, the O2-annealing after N2-annealing reduced the carrier density of the N2-annealed films [closed rhombus symbols in figure 6(a)] to almost the same value as that of the film O2-annealed at 300°C or of the non-annealed (as-deposited) films, when the temperature of O2-annealing was higher than 200°C. On the other hand, addition of N2-annealing increased the carrier density of the O2-annealed films to the state of having values of and temperature dependence of carrier density both similar to those measured after the N2-annealing without pre-annealing in O2 [inverse triangle symbols in figure 6(b)]. These results suggest that the carrier density of the a-IGZO films can reversibly change such that it is increased by N2-annealing and decreased by
O₂-annealing at relatively low temperatures of ≤ 300°C. This is similar to an already reported reversible conductivity change of crystalline Ti₀.₉₄Nb₀.₀₆O₂₋₄ films by O₂- and H₂-annealing at 400°C [21]. The extent of the conductivity change of the a-IGZO films was remarkably wide (5-7 orders of magnitude). To our knowledge, there are few materials that show such a wide-range reversible change of carrier density by annealing at such low temperatures as below 300°C, while irreversible changes are often observed in crystallization, structural reorientation (relaxation), or termination of defects (e.g. oxygen vacancy) by low temperature annealing.

Figure 6. (a) Dependence of carrier density on annealing conditions measured on sputter-deposited a-IGZO films (30 nm in thickness, on glass substrate): [star] with no annealing treatment (as deposited), [circle] with N₂-annealing at various temperatures, [triangle] with O₂-annealing at 300°C, and [rhombus] with O₂-annealing at various temperatures after N₂-annealing at 300°C. A dotted line is indicated as a guide for eyes. (b) Dependences of carrier density [closed symbols] and conductivity [open symbols] on annealing conditions measured on sputter-deposited a-IGZO films (40 nm in thickness, on SiO₂/Si substrate): [circle] with N₂-annealing at various temperatures, [inverse triangle] with N₂-annealing at various temperatures after O₂-annealing at 300°C.

In order to investigate the dynamics of the above-described conductivity change by annealing, we studied thickness dependence of conductance on N₂-annealed a-IGZO films with various annealing time durations. Figure 7 shows thickness dependences of sheet conductance for the films annealed at 300°C in N₂ for 1 hour and 10 hours. For both annealing durations, the sheet conductance linearly increases with the film thickness in a small thickness region, but deviates from the linearity and turns into a state of decreasing with the thickness at 200 nm in the 1 hour annealing case and at 400 nm in the 10 hour annealing case. These observations suggest that some substances which generate conduction carriers like dopants could be created at the film surface by the N₂-annealing, and diffuse into the films with time. A generator of the conduction carriers would not be an injected nitrogen, because annealing in vacuum also increased the conductivity of a-IGZO films, and instead, it would something created by reduction of oxygen such as oxygen deficiency, which works as a donor, or that by removal of excess oxygen as a compensated acceptor.

It is also observed in figure 7 that linear extrapolation of the sheet conductance to zero thickness does not pass through the origin but does a definitely positive intercept (23 nm) at the zero conductance. This observation suggests the existence of a low conductivity layer of about 20 nm in thickness in each of the a-IGZO films. The supposed low-conductivity layer could be a depletion layer generated just above the a-IGZO/SiO₂ interface. Yamaguchi et al estimated such a depletion layer to be 65 nm in thickness [22]. However, it is not likely that the thickness of the depletion layer is more
than 40 nm in the films of the present study, because the thinnest (40 nm-thick) films in figure 7 were still conductive after annealing.

3.2.2. Relation between mobility and carrier density

A simple relation between the Hall mobility ($\mu$) and the carrier density ($N$) with monotonous increase of $\mu$ with increasing $N$ is often observed on amorphous oxide semiconductor films such as of In-Zn-O (a-IZO) with $N \leq 10^{20}$ cm$^{-3}$ [23-25], PLD-deposited a-IGZO [26,27] and Zn-Sn-O (a-ZTO) [28]. The $\mu$-$N$ relations of these materials each can be approximated by a power law of $\mu \propto N^y$, which is observed as a linear relation between log$\mu$ and log$N$. Some models have been proposed for explaining the mechanism of the monotonous increase of $\mu$ with $N$. Nomura et al gave a basic view based on scattering of carriers by potential barriers attributed to randomness of atomic positions, in which the potential barrier height relatively lowers when the Fermi level rises with increase of the carrier density, resulting in an increase of the mobility [1,29]. Recently, Kamiya et al [30,31] formalized this view using an idea of a percolation model in disordered systems proposed by Adler et al [32]. On the other hand, Martins et al [23] interpreted this phenomenon with carrier scattering by defects, like scattering by dislocations in crystalline semiconductors [33].

Figure 8 shows $\mu$-$N$ relations of sputter-deposited a-IGZO films of various thicknesses and preparing conditions. Closed triangle symbols represent data on 300 nm-thick films formed with various O$_2$ contents in the sputtering gas and are replotted in terms of O$_2$ content in the inset. While most of the films were deposited on glass substrates, some films deposited in 1% O$_2$/99% Ar gas (hereafter referred to as "1% O$_2$ gas") were deposited on Si substrates coated with a PECVD-SiN$_x$ film (200-300 nm in thickness), to obtain highly conductive a-IGZO films. Hydrogen molecules or atoms incorporated in the PECVD-SiN$_x$ film diffuse into the a-IGZO film on the SiN$_x$, particularly during annealing even at low temperatures such as 300°C, and thus drastically increase the conductivity of the a-IGZO film. It is predicted that the increase of conductivity by hydrogen incorporation is caused by not only reduction of oxygen but also a chemical doping effect of hydrogen atoms placed at vacant sites [34] or intersites [35,36] in a-IGZO. These a-IGZO films on SiN$_x$/Si substrates were annealed at 300°C in N$_2$, while those on glass substrate were annealed at 300°C in N$_2$ (N$_2$-annealing), in O$_2$ (O$_2$-annealing), or in N$_2$ after N$_2$-annealing (N$_2$-annealing+O$_2$-annealing). Similarly to the amorphous oxide semiconductors described in the above-mentioned previous reports, $\mu$ of the 300 nm-thick a-IGZO films monotonously increase with $N$, and seems to obey a power law of $\mu \propto N^y$. The index $y$ was estimated to be 0.045, which is smaller than the values 0.2-0.5 estimated for other amorphous oxide semiconductors [23,25,28].
Figure 8. Relation between the carrier density $N$ and Hall mobility $\mu$ of sputter-deposited $a$-IGZO films with various thicknesses, substrates, and annealing conditions: [triangle] 300 nm-thick $a$-IGZO films formed in a sputtering gas containing 1, 3, 5, or 10 % O$_2$ on glass substrate or PECVD-SiN$_x$/Si substrate, and treated with O$_2$- or N$_2$-annealing or N$_2$-annealing+O$_2$-annealing at 300°C. The data are also plotted in the inset in terms of O$_2$ content. Among the films deposited with the same sputtering condition, the carrier density of films with N$_2$-annealing is larger than the others, and those with O$_2$-annealing and N$_2$-annealing+O$_2$-annealing are comparable, as notices in figure 6(a). [dot] 30 nm-thick $a$-IGZO films on glass substrate with various sputtering powers (50-400 W), sputtering pressures (0.1-3.0 Pa) and O$_2$ contents in sputtering gas (1-10%). These films were treated with O$_2$- or N$_2$-annealing at 300°C or O$_2$-annealing at various temperatures after N$_2$-annealing at 300°C, [inverse triangle] 40 nm-thick $a$-IGZO films on SiO$_2$/Si substrate annealed in N$_2$ at various temperatures after O$_2$-annealing at 300°C, [open square] 40 nm-thick $a$-IGZO films on SiO$_2$/Si substrate annealed once in N$_2$ at various temperatures.

Closed-dot symbols in the main graph of figure 8 represent data on sputter-deposited 30 nm-thick films on glass substrate. The carrier density of these films were controlled by adjusting the sputtering power (50-400 W), total sputtering pressure (0.1-3.0 Pa), O$_2$ content in the sputtering gas (1-10%) at their depositions. All the films were annealed at 300°C in O$_2$ or N$_2$, and some of them were annealed in O$_2$ at various temperatures after the N$_2$-annealing at 300°C, also to change the carrier density. As seen in figure 8, no apparent dependence of the log$\mu$-log$N$ slopes on the deposition conditions (power, pressure and O$_2$ content) was observed. All the data, regardless of the sputtering conditions, seem to obey a single power-law relation with some degree of fluctuation, and its index ($\gamma \approx 0.042$) is almost the same as that of the data on the 300 nm-thick films. Also 40 nm-thick films on SiO$_2$/Si annealed in N$_2$ at various temperatures after O$_2$-annealing at 300°C show a similar $\mu$-$N$ relation [inverse triangles]. However, 40 nm-thick films on SiO$_2$/Si substrate annealed only once in N$_2$ at 300°C or various temperatures lower than 300°C [open squares] exhibit a steeper slope of log$\mu$-log$N$ ($\gamma \approx 0.18$) than the other films. We suppose that the index in the power law $\mu$-$N$ relation depends on the annealing temperature, where lower annealing temperature make Hall mobility of $a$-IGZO lower than that expected from its carrier density.
3.2.3. Temperature dependences of electrical conductivity, carrier density and Hall mobility

Temperature dependences of electric transport properties of a-IGZO films were investigated to achieve clues to the conduction mechanism. Figure 9 shows the conductivity ($\sigma$) of 40 nm-thick films with various carrier densities in a range from $1 \times 10^{16}$ to $3 \times 10^{19}$ cm$^{-3}$ at room temperature, as a function of inverse temperature ($T^{-1}$). Table 3 shows a list of substrates, annealing conditions, and carrier density values at room temperature for the samples labelled as A to F in figure 9. The conductivity of every a-IGZO film in figure 9 increases with increasing temperature, and temperature dependence of the conductivity becomes weaker as the carrier density increases.

![Figure 9](image1.png)

**Figure 9.** Dependence of the conductivity $\sigma$ on inverse temperature $T^{-1}$ for 40 nm-thick a-IGZO films (sample details are shown in table 3). The inset shows a detailed view above 20 K.

![Figure 10](image2.png)

**Figure 10.** Dependence of the carrier density $N$ on $T^{-1}$ for 40 nm-thick a-IGZO films (sample details are shown in table 3). The solid lines are fitted lines according to the Arrhenius-type thermal activation. The inset shows a view in a wider temperature range for the data of Sample A.

In general, temperature dependence of conductivity in disordered semiconductors exhibits various behaviours originating from different conduction mechanisms according to temperature range. As temperature decreases, the band conduction at high temperature ($\sigma \propto \exp(-T^{-1})$) is followed by the nearest-neighbour hopping (impurity-band) conduction ($\sigma \propto \exp(-T^{-q})$ with a gentler slope than the band conduction), and finally by variable range hopping (VRH) conduction at low temperature ($\sigma \propto \exp(-T^{-1/q})$ where $q = 2$, 3 and 4 for one, two and three dimensional (1D, 2D and 3D) systems, respectively [37]. In figure 9, the conductivity looks proportional to $\exp(-T^{-1})$ at high temperatures of hundreds Kelvin, and deviates from the relation at low temperatures. However, it seems that the conduction of these samples at low temperatures cannot always be attributed to 3D-VRH. Probably, the VRH conduction of Coulomb-gap system or/and other conduction mechanisms contribute to this behaviour.

**Table 3.** Substrates, annealing conditions, and values of the carrier density $N$ at room temperature of the respective a-IGZO samples used in figures 9, 10, and 12.

| Sample | Substrate | Annealing conditions | $N$ at 300 K (cm$^{-3}$) |
|--------|-----------|----------------------|--------------------------|
| A      | SiN$_x$/Si| 300$^\circ$C in N$_2$| $2.7 \times 10^{19}$     |
| B      | Glass     | 300$^\circ$C in 2% D$_2$/98% Ar | $2.8 \times 10^{18}$ |
| C      | Glass     | 300$^\circ$C in N$_2$ | $1.1 \times 10^{18}$    |
| D      | Glass     | 300$^\circ$C in N$_2$ + 150$^\circ$C in O$_2$ | $2.3 \times 10^{17}$ |
| E      | Glass     | 300$^\circ$C in N$_2$ + 170$^\circ$C in O$_2$ | $5.6 \times 10^{16}$ |
| F      | Glass     | 300$^\circ$C in N$_2$ + 200$^\circ$C in O$_2$ | $1.3 \times 10^{16}$ |

Figure 10 shows dependence of the carrier density ($N$) on inverse temperature ($T^{-1}$). While the carrier densities of Samples A and B are independent of temperature, indicating that the samples are
degenerated, those of Samples C, D, E, and F (having carrier density values lower than Samples A and B) show an Arrhenius-type thermal activation being proportional to \( \exp(-T^{-1}) \). Temperature dependence of carrier density is expressed with the donor density \( N_d \) by

\[
\frac{N^2}{N_d - N} = \frac{N_c}{2} \exp \left( -\frac{E_d}{k_B T} \right)
\]

(1)

where \( k_B \) is the Boltzmann constant, \( E_d \) the ionization energy of the donor (i.e., energy difference between the donor state and the conduction band minimum) and \( N_c \) the effective density-of-state of conduction band. If \( N_d \gg N_c \), equation (1) can be approximated as

\[
N \approx \sqrt{\frac{N_c N_d}{2}} \exp \left( -\frac{E_d}{2k_B T} \right)
\]

(2)

\( E_d \) and \( N_d \) of Sample C are estimated by using equation (1) because \( N_d \) could not be so much larger than \( N_c \), and those of Sample D, E, and F are by equation (2). It is assumed here that \( N_c = 2(m^*k_B T/2\pi\hbar^2)^{3/2} \) (where \( m^* \) is the effective mass of electron and \( \hbar \) is equal to Planck's constant \( h \) divided by \( 2\pi \)) does not depend on temperature because the temperature dependence of \( N_c \) should be weaker than \( \exp(-E_d/k_B T) \) at high temperatures. Thus, we employed a value of \( N_c \) at 300 K along with \( m^* = 0.4m_0 \) (\( m_0 \) : the free electron mass) to calculate \( E_d \) and \( N_d \) from the fitted lines drawn in figure 10. The relation between thus estimated \( E_d \) and \( N_d \) values are shown in figure 11(a), where \( N = N_d \) is assumed for the degenerate samples (Samples A and B) as often used for transparent conductive oxide (TCO) films such as ITO [38-40]. This figure indicates that Samples D, E, and F have somewhat deep donors, and \( E_d \) of these decreases with increasing \( N_d \). This lowering of \( E_d \) is probably attributed to an electrostatic shielding effect of electrons loosely bound by impurity ions.

\[\text{Figure 11.} \quad (a) \text{Dependence of the donor ionization energy } E_d \text{ on the donor density } N_d \text{, both calculated from the data shown in figure 10.} \quad (b) \text{Relation between carrier density } N \text{ at 300 K and donor density } N_d \text{ obtained from the data in figure 10. A solid line indicates the relation of } N = N_d. \text{ An arrow indicates the point of } N_d = N_d^{\text{crit}} \text{ above which a-IGZO is degenerate.} \]

Figure 11(b) shows a relation between the carrier density (\( N \)) measured at 300 K and the estimated donor density (\( N_d \)). The solid straight line in the figure indicates the relation of \( N = N_d \) for the degenerate samples. For the non-degenerate samples having \( N_d < 2 \times 10^{18} \text{ cm}^{-3} (\approx N_d^{\text{crit}}) \), deviation from the line of \( N = N_d \) increases as \( N_d \) decreases. It is worth noting that the decrease of \( N_d \) from \( 2 \times 10^{18} \text{ cm}^{-3} \) to \( 6 \times 10^{17} \text{ cm}^{-3} \) (i.e., \( N_d \) changes only by 1/4 times) results in a large reduction of \( N \) by almost two orders of magnitude. This is probably the reason why the conductivity of a-IGZO films is changed so easily and widely by low-temperature annealing, as shown in figure 6.
Since a granular-like structure has been observed by TEM/STEM and SEM in this study, we analyzed the temperature dependence of Hall mobility, based on a hypothesis that the carrier electrons pass through the potential barriers at grain-boundaries by thermionic emission (grain-boundary scattering model) in the a-IGZO films. It has been reported that conductors dominated by the grain-boundary scattering usually show thermal activation of carrier mobility similar to the Arrhenius-type [41,42], which is expressed as

$$\mu = \mu_0 \exp\left(\frac{-\phi}{k_B T}\right) = \mu_1 T^{-1/2} \exp\left(\frac{-\phi}{k_B T}\right), \hspace{1cm} (3)$$

where $\phi$ is the potential barrier height (in the dimension of energy) at grain boundaries and $\mu_1$ a pre-factor. Figure 12 shows application of this model to the Hall mobility data, in which the relation between $\log_\mu T^{1/2}$ and $T^{-1}$ can be fitted with straight lines at high temperatures. The deviation from the straight lines at low temperatures could be due to tunneling conduction through the potential barriers at the grain boundaries [42], and/or distribution of the potential barrier height $\phi$ at the grain boundaries [43]. In figure 13, values of the potential barrier height $\phi$ calculated from the fitting result in figure 12 using equation (3) are plotted as a function of values of the donor density $N_d$ estimated from the result in figure 10 and shown in figure 11. According to Seto [41], the potential barrier height at grain boundaries can be expressed with the donor density $N_d$ and the grain-boundary trap density $Q_t$ as

$$\phi = e^2 Q_t^2 / (8\varepsilon_r \varepsilon_0 N_d), \hspace{1cm} (4)$$

under partially-depleted conditions (i.e., the grain size is larger than $Q_t / N_d$). The solid line in figure 13 is a theoretical curve calculated by equation (4) with $\varepsilon_r = 12$ [44] and $Q_t = 2.2 \times 10^{12}$ cm$^{-2}$, which seems to represent well the estimated dependence using figure 12 and equation (3). A possible reason of the somewhat large deviation at $N_d = 3 \times 10^{19}$ cm$^{-3}$ for Sample A will be discussed in the next subsection.

The value of $Q_t = 2.2 \times 10^{12}$ cm$^{-2}$ is comparable to those reported on other polycrystalline semiconductor films, e.g., $3.0-3.6 \times 10^{12}$ cm$^{-2}$ for silicon [41], $0.5-3.3 \times 10^{12}$ cm$^{-2}$ for InP [45], and $6.7 \times 10^{12}$ cm$^{-2}$ for epitaxial ZnO [46]. For semiconductors with grain-boundary scattering, the pre-factor $\mu_1$ in equation (3) is often considered to be dependent on $\phi$ as

$$\mu_1 = \mu_2 \exp(\gamma \phi), \hspace{1cm} (5)$$
where the pre-factor $\mu_2$ is a constant and $\gamma$ is a coefficient. Orton et al. [47] derived equation (5) by assuming a linear temperature dependence of actual potential barrier height, $\phi_b = (1-\gamma k_\text{B} T) \phi$, as in Si-bycrystals [48], and by substituting $\phi_b$ for $\phi$ in equation (3). A dependence of $\mu_1$ on $\phi$, which was evaluated from the fitting results on Hall mobility in figure 12 using equation (3), is shown in the inset of figure 13. It seems to obey equation (5) indicated by the straight line in the inset. Values of $\gamma$ and $\mu_2$ are estimated to be 21 eV$^{-1}$ and 230 cm$^2$V$^{-1}$s$^{-1}$, respectively. This $\gamma$ value is close to 25 eV$^{-1}$ for polycrystalline CdS films [47].

From the above-described results of the analyses based on the hypothesis of a granular-like structure found in TEM/STEM, SEM, and GISAXS observations, the behaviour of Hall mobility in sputter-deposited a-IGZO films can be explained by the grain boundary scattering model, as well as other proposed models.

3.2.4. Anderson localization

Weak localization behaviour of amorphous oxide semiconductors was discussed by Shimakawa et al. in their study on electronic transport property of amorphous 2CdO-1GeO$_2$ and 2CdO-PbO$_2$ films [49]. Recently, it has been reported that a-IZO films with a large carrier density behave as metallic films even without any magnetic ion, in contrast to that common non-magnetic systems usually show positive magneto-resistance. Figure 15(a) shows magnetic-field ($H$) dependence of the magneto-conductance (inverse of magneto-resistance) up to 150 K. The decrease above 4 Tesla in the temperature increases, which corresponds to decrease of the inelastic scattering time with temperature.

$$\sigma_s = \frac{e^2}{2\pi^2 \hbar}$$

One of the characteristics of weak localization systems is to exhibit negative magneto-resistance even without any magnetic ion, in contrast to that common non-magnetic systems usually show positive magneto-resistance. Figure 15(a) shows magnetic-field ($H$) dependence of the magneto-conductance (inverse of magneto-resistance) $\sigma_s(H)$, measured at various temperatures on the a-IGZO film (Sample A). The a-IGZO film exhibits obvious negative magneto-resistance (positive magneto-conductance) up to 150 K. The decrease above 4 Tesla in the $\sigma_s(H)$ curve measured at 2 K is attributed to the spin-orbit scattering, which contributes to a positive component in magneto-resistance [52]. Figure 15(b) shows relations between $\sigma_s$ and $H^2$ for the respective measurement temperatures. According to the theory, $\sigma_s$ is proportional to $H^2$ at low fields ($H \ll \hbar c/4eL_\text{sc}$) in both 2D and 3D weak localization systems. It is apparent that, for each of the measurement temperatures, $\sigma_s$ is proportional to $H^2$ under low fields, and the field range showing the $\sigma_s \propto H^2$ relation expands as temperature increases, which corresponds to decrease of the inelastic scattering time with temperature.

**Figure 14.** Plot of conductivity $\sigma$ as a function of $T^{1/2}$. The fitted line indicates a linear relation between $\sigma$ and $T^{1/2}$ (3D weak localization behaviour) in the range of 10 to 140 K. The inset shows sheet conductance $\sigma_s$ as a function of $\ln T$. The gradient of the fitted line at low temperatures is $e^2/2\pi^2\hbar$, indicating 2D weak localization behaviour.
expressed as $\tau_n = L_{in}^2/D \propto T^p$, where $D$ and $p$ are the electron diffusion coefficient and a universal parameter, respectively.

According to the above analyses of temperature and magnetic-field dependences of sheet conductance, the sputter-deposited 40 nm-thick a-IGZO film with a relatively large carrier density ($10^{19}$ cm$^{-3}$) shows weak localization like a-IZO films [50]. This suggests that this a-IGZO film is metallic but weakly acts as insulator because of the weak localization effect. This weak localization effect probably leads to overestimation of the potential barrier height at grain boundaries for the sample shown in figure 13, because the dominant scattering mechanism in such a-IGZO with a large carrier density as Sample A is no longer the grain boundary scattering but is the weak localization.

![Figure 15](image.png)

**Figure 15.** (a) Magnetic-field dependence of the magneto-conductance $\sigma(H) - \sigma(0)$ for a 40 nm-thick a-IGZO film (Sample A) at various measurement temperatures. (b) Replot of the magneto-conductance values as a function of the square of the magnetic field.

### 3.3. Optical analyses

#### 3.3.1. UV-VIS-NIR absorption

The optical absorption coefficient, $\alpha$, of amorphous semiconductors can usually be expressed by

$$ahv = B(hv - E_{opt}^{\text{ext}})^2,$$

where $B$ is a coefficient, $h$ Planck's constant, $v$ the photon frequency, and $E_{opt}^{\text{ext}}$ the optical band-gap (Tauc' gap) energy [53,54]. Figure 16 shows for 300 nm-thick a-IGZO films deposited in 1% O$_2$ gas with various annealing conditions (on silica substrates; 300°C N$_2$-annealing, O$_2$-annealing, N$_2$-annealing+O$_2$-annealing and no annealing (as-deposited), and on a SiN$_x$/silica substrate; 300°C N$_2$-annealing), values of $E_{opt}^{\text{ext}}$ and $B$ in equation (6) calculated from $(ahv)^{1/2}$-$hv$ plots of measured spectra, two of which are shown in the inset. $E_{opt}^{\text{ext}}$ shows almost the same values of around 3.1 eV for all the annealed films, but that of the as-deposited film shows a slightly smaller value of 3.0 eV. This shift of $E_{opt}^{\text{ext}}$ is not due to the Burstein-Moss effect, because these $E_{opt}^{\text{ext}}$ values are independent of carrier density, referring to figure 6 and table 3. This $E_{opt}^{\text{ext}}$ shift is probably due to intrinsic change of band-gap through structural relaxation caused by annealing. The coefficient $B$ shows the same tendency as $E_{opt}^{\text{ext}}$: almost the same values for the annealed films but a smaller value for the as-deposited one.

#### 3.3.2. Spectroscopic ellipsometry

We employed the Tauc-Lorentz (TL) model [55,56] to analyze measured ellipsometry spectra of a-IGZO films. The TL model was originally developed to parameterize the optical functions of amorphous materials, and has given excellent fitting results also on crystalline transparent conductive oxide (TCO) films [57,58] and a-IGZO films [15,59]. The present analyses using only the TL model were also successful for most of the a-IGZO films except extremely conductive films with a carrier
density of $10^{20}$ cm$^{-3}$ or more. Figure 17 shows $\Psi(h\nu)$ and $\Delta(h\nu)$ of the ellipsometry spectra (symbols) measured on an a-IGZO film deposited in 1% O$_2$ gas and then received 300°C N$_2$-annealing, along with fitting results using the TL model (solid lines), which represent the measured spectra very well.

Values of the optical bandgap energy ($E_{g\text{TL}}$), refractive index ($n$) and extinction coefficient ($k$) at 1 eV, obtained by the TL model fitting, are listed in table 4. Each $E_{g\text{TL}}$ value is in good agreement with the corresponding optical bandgap energy $E_{g\text{opt}}$ value shown in figure 16, which was estimated from the optical absorption using equation (6) as already described. Values of $k$ must be zero at $h\nu \leq E_{g\text{TL}}$ if an ellipsometry spectrum can be expressed by solely the TL model, because the TL model relies on the assumption that the imaginary part of dielectric constant (corresponding to optical absorption) is extinguished below its bandgap energy. Actually, the measured spectra of the a-IGZO films in table 4 except the H$_2$-annealed film (listed at the bottom of the table) were well expressed by solely the TL model, especially at $h\nu \leq E_{g\text{TL}}$. In other words, absorption below $E_{g\text{TL}}$ indicating a sub-band-gap transition or free carrier absorption was not observed by ellipsometry. The refractive indices of the a-IGZO films except that of the H$_2$-annealed one were $n_r \approx 2.0$ independent of the conditions for annealing and sputtering deposition.

The anomaly described above in the optical constants of the 400°C H$_2$-annealed a-IGZO film having a high carrier density of $1.2 \times 10^{20}$ cm$^{-3}$ is due to free carrier absorption. The fitting by solely the TL model ended up with large deviations from the measured $\Psi(h\nu)$ and $\Delta(h\nu)$ values at wavelengths $\geq 0.9$ μm. Thus we analyzed the ellipsometry spectra of high carrier-density films by a linear combination of the TL model and the Drude model expressed as $\varepsilon(h\nu) = \varepsilon_{TL}(h\nu) + \varepsilon_D(h\nu)$, where $\varepsilon_{TL}$ and $\varepsilon_D$ are the dielectric functions of the TL model and the Drude model, respectively. According to the Drude theory, the complex dielectric function $\varepsilon_D(h\nu)$ can be expressed with the relaxation time $\tau$, carrier density $N$, and mobility $\mu = e\tau/m^*$ as

$$\varepsilon_D = \varepsilon_0 \left\{ \frac{-\hbar^2 e \mu N}{\varepsilon_0 (h\nu)^2 + i\hbar \cdot (h\nu)} \right\}$$

Figure 16. Variation of the optical band gap $E_{g\text{opt}}$ and the coefficient $B$ in equation (6) for 300 nm-thick a-IGZO films with changing annealing treatments. Optical absorption spectra in a $(ah\nu)^{1/2}$ vs. $h\nu$ plot are shown in the inset, for the films with N$_2$-annealing and no annealing treatment (as-deposited).

Figure 17. Ellipsometry spectra of (a) $\Psi(h\nu)$ and (b) $\Delta(h\nu)$ measured with incident angles of 70, 75 and 80 degrees for a 300 nm-thick a-IGZO film deposited in 1% O$_2$ gas on SiO$_2$(100 nm)/n-Si substrate and then N$_2$-annealed at 300°C. Solid lines indicate fitting results using the Tauc-Lorentz model.
for convenience of optical analyses [60]. Consequently, we found that a parameter set of \( m^* = 0.40 m_0 \), \( N = 1.5 \times 10^{20} \text{ cm}^{-3} \), and \( \mu = 20 \text{ cm}^2\text{V}^{-1}\text{s}^{-1} \) gives the best fit to the measured spectra. The value of \( m^* = 0.40 m_0 \) is close to 0.35\( m_0 \) reported on PLD-deposited a-IGZO films by optical model analysis [61]. The optical mobility is close to but slightly larger than the Hall mobility of 18 cm\(^2\text{V}^{-1}\text{s}^{-1}\). This is consistent with the small potential barrier height at grain boundaries of the a-IGZO films with a large carrier density, shown in figure 13.

Table 4. Optical bandgap \( E_{\text{g}}^{\text{TL}} \), and refractive index \( n_\ell \) and extinction coefficient \( k_\ell \) at \( h \nu = 1 \text{ eV} \) estimated from spectroscopic ellipsometry spectra by applying the Tauc-Lorentz model, for 300 nm-thick a-IGZO films deposited in sputtering gas with various O\(_2\) contents and then annealed under various annealing conditions. Exceptionally, a linear combination of the Tauc-Lorentz and the Drude models was used for the fitting of the spectra of the film with H\(_2\)-annealing treatment. The annealing temperature was 300\( ^\circ \text{C} \) for all the samples except those with H\(_2\)-annealing (400\( ^\circ \text{C} \)) and no annealing.

| Sputtering gas | Annealing condition                          | \( E_{\text{g}}^{\text{TL}} \) (eV) | \( n_\ell \) at 1 eV | \( k_\ell \) at 1 eV |
|---------------|---------------------------------------------|------------------------------------|---------------------|-------------------|
| 1% O\(_2\)    | no annealing treatment                       | 3.06                               | 1.98                | 0                 |
|               | N\(_2\)-annealing                           | 3.10                               | 1.97                | 0                 |
|               | N\(_2\)-annealing + O\(_2\)-annealing       | 3.10                               | 1.97                | 0                 |
|               | O\(_2\)-annealing                           | 3.09                               | 1.98                | 0                 |
| 3% O\(_2\)    | N\(_2\)-annealing                           | 3.11                               | 1.98                | 0                 |
| 5% O\(_2\)    | N\(_2\)-annealing                           | 3.12                               | 1.98                | 0                 |
| 10% O\(_2\)   | N\(_2\)-annealing                           | 3.13                               | 1.99                | 0                 |
| 1% O\(_2\)    | H\(_2\)-annealing\(^\ast\) (at 400\( ^\circ \text{C} \) for 40 hours) | 3.10                               | 1.83                | 0.02              |

\(^\ast\)Annealing treatment in 2% H\(_2\)/98% He mixture gas.

4. Discussion

As described in Sec. 3.1, the TEM/STEM, SEM observations and the GISAXS analysis revealed that the sputter-deposited a-IGZO films have columnar-like structures. This suggests the existence of grain boundaries even though the films are amorphous. This is consistent with the fact that the thermal activation behaviour of the Hall mobility observed on the sputter-deposited a-IGZO films [figure 12] can be explained by a model of thermionic emission through potential barriers at grain boundaries. According to the model, the a-IGZO films with a smaller carrier density \( N \) (donor density \( N_d \), to be exact) have higher potential barriers as shown in figure 13, resulting in a smaller carrier mobility \( \mu \). This relation leads to positive correlation between \( \mu \) and \( N \). In fact, such \( \mu-N \) relations have already been observed on some crystalline semiconductor films, e.g., polycrystalline Si [41], S-doped polycrystalline InP [45], Al-/Li-doped epitaxial ZnO [46] and polycrystalline and amorphous In\(_2\)O\(_3\) [62] with low carrier densities compared with those for electrode applications. The mobility of these semiconductor films were well explained by the grain-boundary scattering model. However, theoretically, the mobility of these films should drastically decrease with decreasing carrier density if the donor ionization energy \( E_d \) is almost constant, and the power-law-like \( \mu-N \) relation can be observed in only a narrow range of \( N \).

In the case of the present sputter-deposited a-IGZO films, \( E_d \) increases with decreasing \( N_d \), as shown in figure 11(a), resulting in a significant decrease of \( N \) by a slight decrease of \( N_d \). This causes a moderate decrease of \( \mu \) with decreasing \( N \), thus expanding the range of \( N \) in which the \( \mu-N \) relation obeys the power-law. This may be one possible reason of the characteristic \( \mu-N \) relation of the sputter-deposited a-IGZO films.
5. **Amorphous InO-GaO-ZnO multilayered films**

The family of crystalline InGaO$_3$(ZnO)$_m$ each has a layered crystal structures consisting of stacked InO layers and (Ga,Zn)O layers with random distribution of Ga and Zn. For example, each unit cell of InGaZnO$_4$ (m = 1) has a nine-layer stacks along the c-axis, as shown in figure 18(a). Since the lattice constant $c$ of InGaZnO$_4$ is about 27 Å, the thickness of one constituent layer is estimated to be about 3 Å on average [63]. As shown in figure 18(b), we designed an artificial lattice of amorphous InGaZnO$_4$ with InO and 2(Ga,Zn)O layers stacked alternately, imitating the crystalline InGaZnO$_4$ layer structure. For convenience of the deposition, a stacked of one GaO layer and one ZnO layer were employed in place of the 2(Ga,Zn)O layer. We chose not a simple stacking pattern with a repetition of InO-GaO-ZnO but a pattern with a repetition of InO-GaO-ZnO-InO-ZnO-GaO, because an artificial lattice with the simplest stacking pattern possibly has a polarization in the stacking direction due to a lack of mirror inversion which may affect electrical properti es of the multilayer-films. When the thickness of each constituent layer ($L$) is smaller than 3 Å, which is the above-mentioned average thickness of monolayers in crystalline InGaZnO$_4$, the film becomes in an usual isotropic amorphous state as shown in figure 18(c), and multilayered structures could be realized when $L$ is larger than 3 Å.

![Figure 18](image)

**Figure 18**  (a) Crystal structure of InGaZnO$_4$. (b) Designed structure of multilayered [GaO/ZnO/InO/ZnO/GaO/InO]$_n$ film ($n$: repetition number) when the constituent layer thickness $L$ is large enough (>3 Å). (c) Schematic drawing of an isotropic amorphous In-Ga-Zn-O film to be formed by the same method as that for the multilayered film shown in (b) when $L$ is too small to form a continuous monolayers.

The deposition rate for each constituent layer was estimated from film thicknesses measured as a function of the number of input laser pulses on test samples deposited on a thermally-grown SiO$_2$ (100 nm)/Si substrate. Figure 19 shows XRR patterns for GaO thin layers deposited with various number of input laser pulses (60-840 pulses). The number of fringes on the XRR profiles increases with increasing the number of input pulses. As the number of fringes corresponds to the thickness, the film thickness for each of the test samples was estimated from the corresponding XRR pattern (fitting results for GaO layers are shown in the figure). Thus obtained film thicknesses are plotted against the number of input laser pulses in figure 20, along with the results on InO and ZnO. For InO and GaO, in the thickness range up to 80 Å, the relations between thickness and the number of input pulses can be fitted almost with the same linear function. A thickness offset of the fitted line at zero pulse would correspond to a thin layer deposition during the pre-deposition step for target cleaning, due to the
existence of a slight number of particles leaking from around the shutter in the PLD chamber. We estimated the deposition rate common to InO and GaO from the gradient of the fitted line. On the other hand, the deposition rate of ZnO shows two different values depending on the thickness; the lower value for thicknesses above 20 Å. This could arise from crystallization of ZnO, because it is well-known that ZnO films deposited by sputtering or evaporation are easily crystallized even at room temperature [64].

Figure 19. X-ray reflectivity (XRR) profiles of GaO layers deposited with various numbers of input laser pulses on SiO$_2$(100 nm)/Si substrates. Solid lines indicate fitting.

Figure 20. Dependences of film thickness on the number of input laser pulses for InO, GaO and ZnO layers.

First, [GaO/ZnO/InO/ZnO/GaO/InO]$_n$ multilayered films with a total thickness of 54 nm were formed by n-times repetition of a deposition of the InO-GaO-ZnO-InO-ZnO-GaO layer on glass substrates with $L = 3$, 4.5 and 6 Å. In XRD patterns of these samples, no peak from crystalline InO, GaO or ZnO was found, which indicates that each constituent layer remains amorphous. Instead, as shown in figure 21(a), broad peaks were observed at very low angles of 5.8°, 7.1°, and 7.5° for the
multilayered films with \( L = 3, 4.5 \text{ and } 6 \text{ Å} \), respectively. These peaks each can be assigned to a Bragg peaks of the respective artificial lattices. For instance, the unit lattice parameter of the multilayer with \( L = 4.5 \text{ Å} \) is calculated as \( 6 \times L = 27 \text{ Å} \), while the peak observed at 7.1º indicates a spacing of about a half of 25 Å. Thus, this XRD peak is in agreement with the expected unit lattice parameter. Similarly, the peak at 5.8º for the multilayered film with \( L = 3 \text{ Å} \) (unit lattice parameter: 18 Å) corresponds to a spacing of about 15 Å, and the peak at 7.5º for the multilayered film with \( L = 6 \text{ Å} \) (unit lattice parameter: 36 Å) corresponds to a spacing of about 12 Å, which is exactly one-third of the unit lattice parameter.

Figure 21(b) shows a reciprocal space map of the diffraction at 7.1º of the multilayered film with \( L = 4.5 \text{ Å} \). The spreads of the diffraction intensity along the vertical-axis \( (2\theta/\omega) \) and that along the horizontal-axis \( (\Delta\omega) \) indicate fluctuations in periodicity and that in orientation of the lattice, respectively. As can be seen in the map, the fluctuation in lattice periodicity is fairly large, while that in lattice orientation is very small. This observation suggests that highly parallel stacking of the constituent layers were realized, even though the actual thickness of the constituent layers fluctuated. It is thus confirmed that amorphous artificial lattices composed of InO, GaO and ZnO constituent layers were successfully formed.

Cross-sectional TEM observation of this multilayered film (\( L = 4.5 \text{ Å} \)) was carried out. As shown in figure 22, an obvious layered structure was confirmed. The dark and bright layers correspond to InO and 2(Ga,Zn)O layers, respectively, and the thickness of each layer is close to the intended thickness. This observation is consistent with the XRD results described above. Since the tolerance of the observation conditions was narrow for such thin layers and the conditions were optimised for an area around the film/substrate interface, the layered structure looks blurred at the upper area of the film. Additionally, surface roughness of the films slightly increases with increasing film thickness, resulting in an unclear layered structure at the upper area of the film. For a multilayered film with thicker composition layers of \( L = 15 \text{ Å} \), each constituent layer can be observed clearly even in the upper area.
of the film, as shown in figure 23(a). In this film, a definite 2D structure was attained, as can be seen in figure 23(b).

Subsequently, Hall measurement samples were prepared from 50-60 nm-thick [GaO/ZnO/InO/ZnO/GaO/InO]$_n$ multilayered films having various $L$ values. Since the actual constituent layer thickness was found to become slightly smaller than the nominal thickness as mentioned above, $L = 3.5$ Å was employed instead of $L = 3$ Å. Figure 24 shows dependences of the Hall mobility and the carrier density on $L$. The dependence of the Hall mobility on $L$ exhibits curious behaviour, while the carrier density shows simple and monotonous increase with $L$. We assume that the multilayered film with $L = 1$ Å possesses an isotropic amorphous structure like that shown in figure 18(c), while the films with $L > 3$ Å have a 2D multilayer structures forming an artificial lattices as seen in figure 22. Thus expected is a difference in the Hall mobility between them. However, the Hall mobility was almost independent of $L$ up to 6 Å, i.e., regardless of the layer structure, with the values around 4 cm$^2$V$^{-1}$s$^{-1}$. This Hall mobility value seems reasonable for uniform a-IGZO films under this PLD condition (KrF excimer laser power density of approximately 5 Jcm$^{-2}$), compared to the reported values of about 2 and 10 cm$^2$V$^{-1}$s$^{-1}$ for a-IGZO films by PLD with 2 and 9 Jcm$^{-2}$, respectively [27]. This observation suggests that, at least in this small thickness range, the carrier transport in the lateral direction of the constituent layers is almost comparable with that in the vertical direction. Nearly isotropic conduction of InGaZnO$_4$ despite its highly anisotropic 2D layer-structure has been theoretically predicted with first-principle calculation [65], which is consistent with the presently observed behaviour of the Hall mobility for $L \leq 6$ Å. Furthermore, the imperfection of 2D structure observed in the cross-sectional TEM observation (figure 22) may have affected the Hall mobility to some degree.

![Figure 23](image_url)

Figure 23. (a) Cross-sectional TEM image of a multilayered [GaO/ZnO/InO/ZnO/GaO/InO]$_6$ film with $L = 15$ Å on SiO$_2$/Si substrate. Carbon and Metal (Cr) films were deposited on the film to define the film surface. (b) Expanded view of the cross-sectional TEM image in (a).
As $L$ increases beyond 6 Å, the Hall mobility shows a drastic increase in the range of $L \leq 15$ Å. Such an increase in the Hall mobility could be attributed to enhancement of the character of InO of having a higher carrier mobility than ZnO, GaO and InGaZnO$_4$, with the increase in the layer thickness. It is also noteworthy that the peak Hall mobility of 23 cm$^2$V$^{-1}$s$^{-1}$ is comparable to or even slightly higher than those reported on epitaxial InGaZnO$_4$ films [66]. Also reduction of the imperfection of 2D structure shown in the TEM observation (figure 23) may have contributed to this rise of the Hall mobility.

Above $L = 15$ Å, the Hall mobility abruptly decreases with increasing $L$, which is presumably due to the increase of the roughness of each constituent layer with increasing $L$, caused by crystallization of ZnO layers accompanied by the ZnO deposition rate change shown in figure 20. The crystallization of ZnO layers would lead to facet formation and enlarge the roughness at the interfaces between layers, resulting in deterioration of the periodicity of the artificial lattice. The interface roughness and the deterioration of periodicity should enhance carrier scattering.

The monotonous increase of the carrier density in the whole $L$ range [figure 24] could be attributed to enhancement of the above-mentioned indium oxide's character in InO layers, because amorphous In$_2$O$_3$ films usually show a carrier density value of the order of $10^{20}$ cm$^{-3}$. Consequently, $L$ of 10-15 Å is an optimum condition to realize a high conductivity in the plane of the multilayered film.

Multilayered films of InO-GaO-MgO were also formed by substituting MgO for ZnO, and their carrier density and Hall mobility were measured. As shown together in figure 24, the carrier density of the InO-GaO-MgO multilayered films increases with $L$, and the Hall mobility is almost independent of $L$ in the range of $L = 1$ to 6 Å, similarly to those of InO-GaO-ZnO multilayered films. However, the carrier density are remarkably small and the Hall mobility are rather small, compared to those of InO-GaO-ZnO multilayered films. These observations are consistent with the difference in the carrier density between InGaMgO$_4$ and InGaZnO$_4$ ceramics [67] and with the larger effective electron mass of InGaMgO$_4$ than InGaZnO$_4$ [65] This suggests that ZnO layers play a role of a carrier supplier and provide a large carrier mobility in InGaZnO$_4$, compared to MgO layers in InGaMgO$_4$. Furthermore, we formed 50 nm-thick YO-GaO-ZnO multilayer films, using yttrium oxide (YO) layers in place of InO layers, with $L$ of 3.5-6 Å. The samples had a resistivity too high to measure the Hall effect. This result confirms that InO layers are further important in carrier supply and/or provision of a large carrier mobility in InGaZnO$_4$.

6. Summary
We investigated microscopic structures, electrical and optical properties of sputter-deposited a-IGZO films, and discussed correlations among them.
TEM/STEM and SEM observations revealed that the sputter-deposited a-IGZO films consist of a columnar structure, which was confirmed by GISAXS analysis. Gas-adsorption analysis revealed, however, that the sidewall surfaces of the columnar grains are little active in adsorbing ambient gas molecules and thus, the grain boundaries observed by cross-sectional TEM/STEM are not open-pores. XAFS analysis indicated imperfection in In-O coordination in the a-IGZO films.

The conductivity of the sputter-deposited a-IGZO films exhibits a change as large as seven orders of magnitude almost reversibly between N2- and O2-annealings even at a temperature as low as 300°C, such that the high conductivity state obtained by N2-annealing turned into the low conductivity state by O2-annealing and vice versa. The sputter-deposited a-IGZO films exhibit a power-law relation between the Hall mobility $\mu$ and the carrier density $N$. Temperature dependence of $N$ in the sputter-deposited a-IGZO films with $N \leq 1 \times 10^{18} \text{cm}^{-3}$ shows the Arrhenius-type thermal activation at temperatures around and below room temperature. The ionization energy of donor $E_d$ increases with decreasing the donor density $N_d$ and reaches 250 meV at $N_d \approx 6 \times 10^{17} \text{cm}^{-3}$, resulting in a small $N$ value of $1 \times 10^{15} \text{cm}^{-3}$ at room temperature. For a-IGZO films having widely different conductivities, temperature dependence of $\mu$ suggests Arrhenius-type-like thermal activation above 150-200 K. This behaviour can be explained by a model of thermionic emission through potential barriers at grain boundaries (grain-boundary scattering model), which is consistent with the TEM/STEM and SEM observations.

The optical band-gap energy of the sputter-deposited a-IGZO films showed a difference between before and after annealing but did not change with annealing conditions, in contrast to a significant dependence of the carrier density on the annealing conditions. By spectroscopic ellipsometry analysis, electron effective mass $m^*$ of the sputter-deposited a-IGZO films was estimated to be 0.4$m_0$, which is close to the reported value on PLD-deposited a-IGZO films (0.35$m_0$).

Further, multilayered films composed of amorphous InO, GaO and ZnO (or MgO) constituent layers were formed using a computer-controlled PLD system, to imitate the layered structure of the InGaZnO$_4$ homologous phase. An artificial periodic lattice structure was realized in each of 54 nm-thick [GaO/ZnO/InO/ZnO/GaO/InO]$_n$ multilayer films with the single constituent layer thickness $L = 3, 4.5$ and $6 \text{ Å}$, which was confirmed by superlattice peaks in XRD profiles and cross-sectional TEM images. The Hall mobility of [GaO/ZnO/InO/ZnO/GaO/InO]$_n$ was almost constant for $L \leq 6 \text{ Å}$, and increased for $6 \text{ Å} \leq L \leq 15 \text{ Å}$, suggesting that the conduction is rather isotropic even in the multilayer structures when $L$ is small, and 2-dimensional conduction in InO layers is enhanced when $L$ is larger. Substitution of MgO and YO layers for ZnO and InO, respectively, resulted in drastic increase of resistivity, suggesting that ZnO and InO layers each play an important role in the electrical conduction in InGaZnO$_4$.

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