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Factors controlling electron transport properties in transparent amorphous oxide semiconductors

Hideo Hosono [a,b,c,*], Kenji Nomura [b], Youichi Ogo [b,c], Tomoya Uruga [d], Toshio Kamiya [b,c]

[a] *Frontier Research Center, Tokyo Institute of Technology, Nagatsuta, Midori-ku, Yokohama 226-8503, Japan*
[b] *ERATO-SORST, Japan Science and Technology Agency, Frontier Research Center, Tokyo Institute of Technology, Nagatsuta, Midori-ku, Yokohama 226-8503, Japan*
[c] *Materials and Structures Laboratory, Tokyo Institute of Technology, Midori-ku, Yokohama 226-8503, Japan*
[d] *SPring-8, Japan Synchrotron Radiation Research Institute, 1-1-1 Kouto, Mikazuki-cho, Hyogo 679-5198, Japan*

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Abstract

Metal cation species and post-annealing treatments were extracted as the primary factors affecting the electron transport properties in transparent amorphous oxide semiconductors (TAOS). Amorphous (a-) In–Ga–Zn–O (a-IGZO) thin films were taken as an example to examine the effects of deposition conditions and thermal annealing. Two groups of a-In–GZO films (deposited at the 'optimized' and 'unoptimized' conditions) were deposited by changing laser pulse energy used for pulsed laser deposition. The electron transport properties of the as-deposited films fabricated at the unoptimalized condition were improved by thermal annealing to a level which is almost the same as that in the films deposited at the optimized condition. The temperature range effective for the improvement is ⩾300 °C, which is fairly lower than the on-set temperature (∼500 °C) for crystallization. To extract the effects of constituent metal cations, transport properties of a-Sn–Ga–Zn–O (a-SGZO) films and their TFTs were compared with those of the a-IGZO. Comparison of the TFT performances between the a-IGZO and a-SGZO channels revealed that the In-based system has much better performances when the device is fabricated without intentional annealing. Much stronger absorption tail was seen for the as-deposited a-SGZO thin films, implying the formation of a low valence state, Sn^{2+}, and relevant defect states locating near the conduction band minimum deteriorate the TFT performances.
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1. Introduction

Transparent amorphous oxide semiconductors (TAOS) have been attracting attention as channel layers of thin film transistors (TFTs) since the report of a flexible, high performance TFT fabricated on a plastic substrate employing an amorphous In–Ga–Zn–O (a-IGZO) thin films by pulsed laser deposition (PLD) in the end of 2004 [1,2]. The TAOS TFTs have several advantages over TFTs based on other semiconductors; they can be fabricated on plastic substrates at a low temperature (below 150 °C) by physical vapor deposition methods such as conventional sputtering [3], and field effect motilities of $>10\ cm^2\ (V\ s)^{-1}$ are obtained at a high reproducibility with a high uniformity. These excellent performances originate from the unique characteristics of TAOS which is the first amorphous semiconductor composed of highly ionic chemical bonds [4,5]. The Hall mobility in TAOS is comparable to that in the corresponding crystalline phases and no Hall voltage sign anomaly, which is commonly observed in the conventional amorphous semiconductors, has been observed [5,6]. These

* Corresponding author. Address: Frontier Research Center, Tokyo Institute of Technology, Nagatsuta, Midori-ku, Yokohama 226-8503, Japan. Tel.: +81 45 924 5359; fax: +81 45 924 5339.
E-mail address: hosono@msl.titech.ac.jp (H. Hosono).

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electron transport properties come from (i) the large overlap between vacant s-orbitals of neighboring heavy metal cations at the conduction band bottom and (ii) the small tail state density [4,5]. Since the tail state density is low, one can lift the Fermi level to above the mobility gap by carrier doping, realizing the degenerate state at > the carrier concentration $\sim 4 \times 10^{18}$ cm^{-3}. The leveling off of Fermi level by doping observed in a-Si:H is not observed in TAOS, and this observation may be understood by remembering that validity of the Mott–Street model [7] is based on covalent bonded amorphous materials.

Formation of ionic amorphous materials such as TAOS needs a extremely high cooling rate, i.e., they cannot be obtained in the form of bulk, but can be fabricated as a thin film by using physical vapor deposition techniques. It is thus considered natural that a chemical species and/or a structure, which is stable at higher temperatures but is unstable at RT, is frozen in the as-deposited thin film and relaxes to a more stable structure upon thermal annealing, leading to an appreciable change in the electron transport properties. Clarifying the thermal annealing effect is essentially important for understanding the intrinsic nature of TAOS toward a device application. In this paper, we report the preliminarily experimental results on the effects of the thermal annealing and the role of constituent heavy metal cation species. The TAOS thin films used were a-In–Ga–Zn–O (a-IGZO) and a-Sn–Ga–Zn–O (a-SGZO). According to the working hypothesis [4], candidate materials for high mobility TAOS are required to have heavy metal cations with $(n-1)d^{10}ns^0$ electronic configurations (where the principal quantum number $n \geqslant 5$) as a major constituent. Although both of In^{3+} and Sn^{4+} having the same electronic configuration $[Kr](4d)^{10}(5s)^0$ meet this requirement, no comparison in TFT/electronic transport properties between them has been reported to date.

2. Experimental

a-IGZO and a-SGZO thin films were prepared by PLD (laser source KrF) using ceramic targets of crystalline $InGaZnO_3$ and a composite of SnO_2, Ga_2O_3, and ZnO with the chemical composition of $SnGaZnO_{3.5}$, respectively. The partial O_2 pressures during the deposition were chosen to be 1.0–7.0 Pa to control carrier concentration from $<10^{15}$ to 10^{20} cm^{-3}. No intentional heating of the substrate was performed. Thin films (100–150 nm thick) were deposited on silica glasses for Hall effect and optical measurements. Hall voltage measurements were carried out using the van der Pauw configuration with an AC modulation of a magnetic field at 0.5 T at RT. Sputtered gold electrodes were used for ohmic contacts. Films with 40 nm thickness were deposited on thermally oxidized silicon wafers as channels for TFTs. Bottom gate TFTs were fabricated on SiO_2 (gate insulator, 150 nm^t)/Si substrates (gate electrode), and Au/ITO layers were used as the source and drain contacts. The TFT structures were defined by photolithography and lift-off. The channel width (W) and length (L) were 300 and 50 μm, respectively. Output and transfer characteristics were measured using a Keithley 4200 semiconductor characterization system.

The as-deposited films and the as-fabricated TFTs were annealed at varied temperatures up to 500 °C. The amorphous structure of each sample was confirmed by glancing-incidence X-ray diffraction using a high power X-ray source (50 kV × 300 mA), and cross-sectional TEM observations and selected area electron diffraction were carried out for some representative films. X-ray absorption measurements were performed at a synchrotron radiation facility (SPring-8) and extended X-ray absorption fine structures (EXAFS) were extracted by a standard method and analyzed with a code REX 2000 (Rigaku, Japan). Corresponding crystalline films were used as references to determine the phase-shift parameters. The chemical state of constituent cation in some samples was measured by X-ray photoelectron spectroscopy.

3. Results

The a-IGZO films deposited by different laser power energy densities showed a large variation in Hall mobility (μ_{Hall}), i.e., the Hall mobility of the film (carrier density of 10^{17} cm^{-3}) deposited at a laser energy of 2 J cm^{-2} was $\sim$0.9 cm^2 (V s)$^{-1}$, while that of the film deposited at the optimized laser energy of 9 J cm^{-2} with the same carrier density was $\sim$9 cm^2 (V s). Fig. 1(a) shows optical absorption spectra of a-IGZO films with different thermal histories. The as-deposited film shows an absorption tail in the 2.0–3.7 eV region. When the film is annealed at $\leqslant$200 °C, the absorption tail remains unchanged, but abruptly decreases when annealed at 300 °C. Further gradual decrease is observed by annealing at higher temperatures. The μ_{Hall} value is conspicuously improved from 0.9 to $\sim$4 by annealing at 300 °C and increases up to $\sim$8 cm^2 (V s)$^{-1}$ at $\geqslant$500 °C (Fig. 1(b)). These results appear that reduction in the absorption tail is parallel to the improvement of μ_{Hall}, i.e., the μ_{Hall} is improved by the reduction of the absorption tail and the critical temperature at which the large change occurs is $\sim$300 °C.

Fig. 2 shows the TFT characteristics of a-IGZO TFTs with different thermal histories. Although the field effect mobility (μ_{sat}) estimated from the saturation current and S value (sub-threshold voltage swing) of the TFT using the as-deposited channel are rather poor (Fig. 2(b)), the device thermally annealed at 300 °C exhibits a good performance (Fig. 2(c)), which is comparable to that using the film deposited at the optimized condition as the channel (Fig. 2(a)).

Fig. 3(a)–(c) shows the EXAFS radial distribution function for each metal cation in the a-IGZO thin films as-deposited and annealed at 400 °C. Structural parameters extracted from the EXAFS analyses are listed in Table 1. No significant difference is seen in the coordination number around a cation, the cation–oxygen distances, or the cation–cation distances between the as-deposited and the

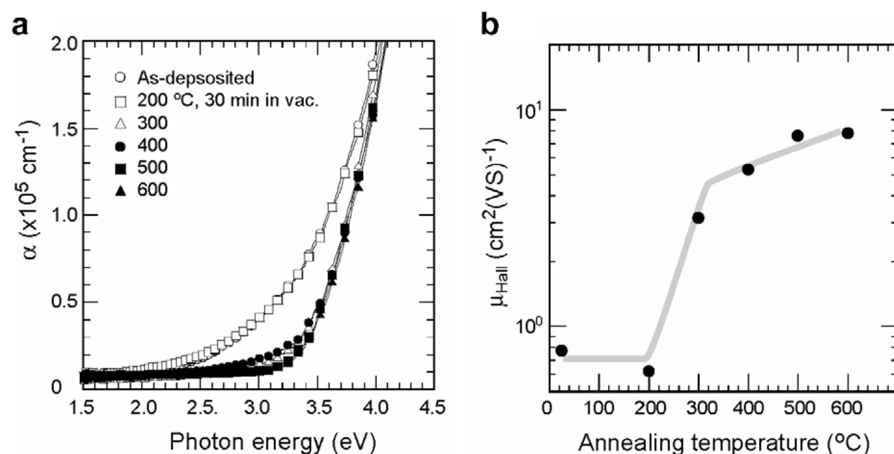

Fig. 1. Effects of thermal annealing on (a) the optical absorption and (b) Hall mobility of a-IGZO thin films deposited at an unoptimized condition. Annealing was performed in air and the holding time at each temperature was 30 min. The carrier concentration before annealing was 2×10^{19} cm^{-3}.

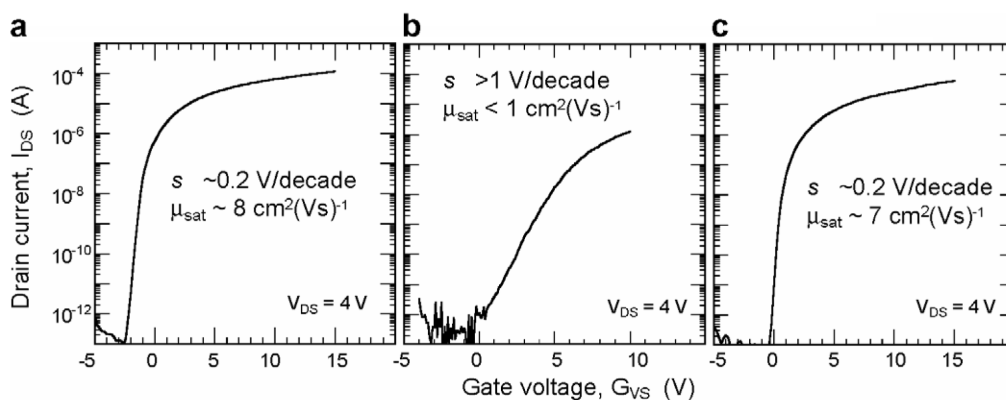

Fig. 2. Comparison of TFT performances using (a) as-deposited, optimized channel, (b) as-deposited, unoptimized channel, and (c) annealed (b) at 300 °C for 0.5 h in air.

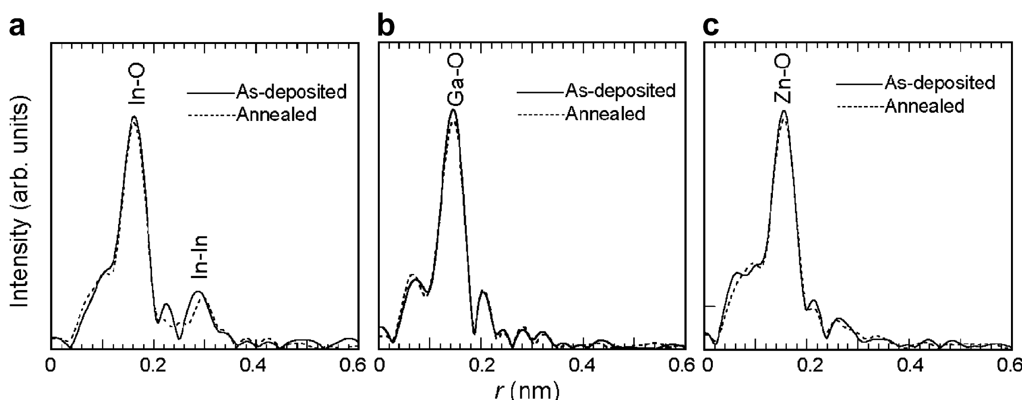

Fig. 3. Radial distribution function in a-In–GZO films as-deposited (solid lines) and annealed at 400 °C (dotted lines) for (a) In, (b) Ga, and (c) Zn obtained from EXAFS measurements.

annealed films. This means that neither the change in the coordination number around each cation nor distance between a metal and an oxygen is involved in the structural relaxation occurring during the annealing.

Next, we compared the optical absorption spectra and TFT characteristics of the optimized a-IGZO with those of a-SGZO. The deposition condition for the a-SGZO films was optimized at room temperature using a μ_{sat} as the measure. A distinct difference was observed in the absorption spectra and TFT performances. The a-IGZO TFT exhibited $\mu_{sat} = 8\ cm^2\ (V\ s)^{-1}$ and $S = 0.2\ V\ (decade)^{-1}$, whereas the a-SGZO TFT did not exhibit a clear pinch-off. Fig. 4 shows the optical absorption spectra of the as-deposited and annealed films plotted in a logarithmic scale. The

Table 1
The local structural parameters for as-deposited and annealed a-In–GZO films evaluated by EXAFS measurements

	In–O		Ga–O		Zn–O	
	r (nm)	*N*	*r* (nm)	*N*	*r* (nm)	*N*
As-deposited	0.212	5.0	0.193	4.2	0.191	5.3
Annealed	0.212	5.6	0.193	4.3	0.191	5.1

Annealing was performed at 400 °C for 0.5 h.

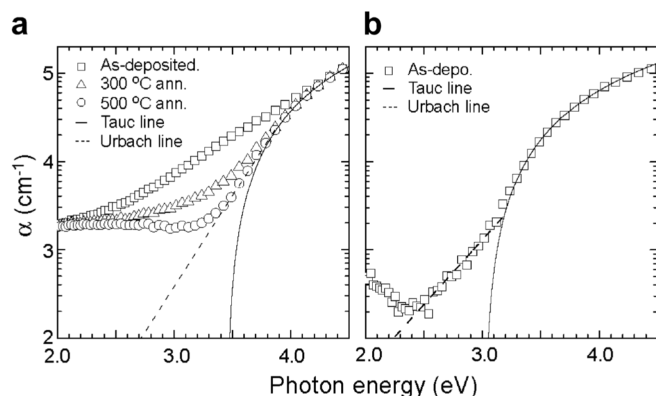

Fig. 4. Optical absorption spectra of (a) a-SGZO and (b) a-IGZO films with different thermal histories. Samples used were deposited at the optimized condition for each sample. Annealing was carried out in an ambient atmosphere.

absorption tail intensity in the SGZO is larger by an order of magnitude than that in the IGZO for the as-deposited films. The tail intensity in the SGZO is reduced by annealing, but the intensity in the best film annealed at 500 °C is still larger than that in the as-deposited a-IGZO film. It was also observed that the performance of the a-SGZO TFTs was much improved by annealing at temperatures ⩾400 °C as reported in a previous paper [8].

4. Discussion

In a previous paper [9], we evaluated the energy width of the conduction band tail states from conductivity-temperature data on the a-IGZO films with different carrier concentration, reporting that the energy width in a-IGZO is 7–20 meV, depending on the deposition condition (that is, laser power density for ablation) and the magnitude is distinctly smaller than that reported in a-Si:H (∼55 meV in Urbach tail width). The present work examined the effect of thermal annealing on the electron transport properties and optical absorption tails. Hall and field effect motilities in the films deposited at the unoptimized condition is much improved by thermal annealing at temperatures ⩾300 °C, which is lower by ∼200 °C than the on-set temperature of crystallization (∼500 °C) [2]. An excellent correlation was found among the Hall mobility, field effect mobility, and the reduction in the absorption tail intensity for the unoptimized a-IGZO films with increasing the annealing temperature, and these properties approach to the level that is attained for the as-deposited, optimized a-IGZO. The EXAFS results suggested that a local rearrangement of ions which does not involve change in the coordination number around each cation or metal–oxygen bonding separation is the primary origin for the observed changes. In the a-IGZO system, the conduction band bottom, which works as electron path way, is primarily composed of three-dimensionally connected In 5s-orbitals [10]. Thus, a plausible structural relaxation is required to resulting in the enhancement of connectivity and/or overlap among the In 5s-orbitals, It was observed that the activation energies of the Hall mobilities in the as-deposited, unoptimized films had larger values than the annealed films[9], indicating that the thermal annealing reduces the density of the shallow localized states beneath the conduction band minimum. At the present stage, we cannot identify the entity of absorption tail appearing in the as-deposited film and the energy levels of the gap states. However, the tail states controlling the Hall mobility should be located near the mobility gap. Heavily distorted In–O polyhedra and a specific oxygen vacancy are plausible candidates. Improvement of electron transport properties observed here is similar to that in amorphous metals and glassy semiconductors. Structural relaxation upon thermal annealing at a temperature much below the on-set of crystallization favors the electronic conduction. Further effort employing the technique used for a-Si:H is obviously needed to get more information about the tail states.

Finally, comparison between a-IGZO and a-SGZO is considered. The absorption tail state intensity in the a-SGZO is larger by two orders of magnitude than that in the a-In-GZO compared at the as-deposited state. This conspicuous difference may be tentatively attributed to the difference in the thermodynamic stability of the valence states of the constituting metal cations, i.e., the difference between a lower valence state (2+) and a higher valence state (4+) is minimal for Sn among the constituting metals. XPS revealed that a small peak responsible for Sn^{2+} was observed at the position of ∼3 eV from the Fermi level(the conduction band bottom), i.e., the above of the valence band top, for the as-deposited sample and the intensity of this peak was distinctly reduced by annealing at 600 °C [11]. It is well known that a Sn^{2+} having $[Kr](5d^{10})(5s^2)$ configuration gives absorption at an energy range much lower than that of Sn^{4+}. In general, the coordination number around a Sn^{2+} ion is lower than that of a Sn^{4+}. So, we may suppose that thermal annealing induces atomic rearrangements involving a displacement of an oxygen ion from a neighboring coordination sphere to that of a Sn^{2+} ion, which accompanies the oxidation to a Sn^{4+} state. The electro-neutrality is kept by incorporating O^{2-} ions from O_2 molecules adsorbed on the surfaces. Anyway, we may suggest that valence-changeable heavy metal cations are not appropriate for flexible TFT applications because thermal annealing at a temperature >∼300 °C is requisite to have improved performances.

A transparent TFT is a heart of transparent electronics [12,13] and TAOS is being expected as a promising candi-

date of channel semiconductor in high performance TFTs [14–17] for OLEDs and e-papers. We consider the understanding and control of the tail states in TAOS is a key for realizing these applications. Since the TAOS is a novel class of semiconductors (i.e., ionic amorphous materials), it is obvious that accumulation of basic data and introduction of approach unique to this system are needed.

5. Summary

We examined the effects of thermal annealing on the electron mobility in a-IGZO and a-SGZO films deposited by pulsed laser deposition. The results obtained are summarized as follows:

(1) The Hall mobility and field effect mobility in a-IGZO thin films deposited at the unoptimized condition were much improved by annealing at temperatures $\geqslant 300$ °C and approached to the values of the as-deposited optimized films.
(2) The threshold annealing temperature ($\sim$300 °C) for the improvements in the transport properties for the unoptimized a-IGZO films was much lower than the on-set temperature ($\sim$500 °C) of crystallization.
(3) The intensity of absorption tail appearing in 2.0–3.7 eV in a-In-GZO was distinctly reduced by annealing at temperatures $\geqslant 300$ °C and the extent of this reduction was parallel to the improvement of the mobility.
(4) No significant change in the coordination number around each cation or cation–oxygen bond distance by annealing was observed in EXAFS measurements.
(5) The performances of a-SGZO TFTs are much lower than those of a-IGZO, especially for the a-SGZO channels as-deposited and annealed at $\leqslant 400$ °C. The absorption tail intensity in the SGZO was larger by an order of magnitude than that in the IGZO. This difference is attributed to the formation of Sn^{2+} and the relevant defects. It is considered that valence-changeable heavy metal cation-based TFTs are not appropriate for flexible TFT applications.

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References

[1] K. Nomura, H. Ohta, A. Takagi, T. Kamiya, M. Hirano, H. Hosono, Nature 432 (2004) 488.
[2] K. Nomura, A. Takagi, H. Ohta, T. Kamiya, M. Hirano, H. Hosono, Jpn. J. Appl. Phys. 45 (2006) 4303.
[3] H. Yabuta, M. Sano, K. Abe, T. Aiba, T. Den, H. Kumomi, K. Nomura, T. Kamiya, H. Hosono, Appl. Phys. Lett. 89 (2006) 112123.
[4] H. Hosono, M. Yasukawa, H. Kawazoe, J. Non-Cryst. Solids 203 (1996) 334;
H. Hosono, J. Non-Cryst. Solids 352 (2006) 851.
[5] S. Narushima, M. Orita, M. Hirano, H. Hosono, Phys. Rev. B 66 (2002) 035203;
S. Narushima, H. Hosono, J. Jisun, T. Yoko, K. Shimakawa, J. Non-Cryst. Solids 274 (2000) 313.
[6] K. Shimakawa, S. Narushima, H. Hosono, H. Kawazoe, Philos. Mag. Lett. 79 (1999) 755;
K. Shimakawa, H. Hosono, N. Kikuchi, H. Kawazoe, J. Non-Cryst. Solids 227–230 (1998) 513.
[7] R.A. Street, Phys. Rev. Lett. 49 (1982) 1187;
J. Robertson, Phys. Rev. B 31 (1985) 3827.
[8] Y. Ogo, K. Nomura, H. Yanagi, T. Kamiya, M. Hirano, H. Hosono, Phys. Status Solidi (a), accepted for publication.
[9] K. Nomura, T. Kamiya, H. Ohta, K. Shimizu, M. Hirano, H. Hosono, Phys. Status Soldi (a), accepted for publication.
[10] K. Nomura, T. Kamiya, H. Ohta, T. Uruga, M. Hirano, H. Hosono, Phys. Rev. B 75 (2007) 035212.
[11] Detailed discussion based on these data will be published in a separate paper.
[12] R.L. Hoffman, B.J. Norrism, J.F. Wager, Appl. Phys. Lett. 82 (2003) 1117;
R.E. Presley, D. Hong, H.Q. Ching, C.M. Hung, R.L. Hoffman, J.F. Wager, Solid State Electron. 50 (2006) 500.
[13] H. Hosono, Thin Solid Films 615 (2007) 6000.
[14] R. Martin et al., J. Non-Cryst. Solids 352 (2006) 1471;
E. Fortunate et al., Adv. Mater. 17 (2005) 590.
[15] P. Görrn et al., Adv. Mater. 18 (2006) 738;
P. Görrn et al., Appl. Phys. Lett. 90 (2007) 063502.
[16] H.-N. Lee et al., SID 07 Digest 38 (2007) 1826.
[17] M. Ito et al., IEICE Trans. Electron. E90-c (2007) 2105.