Journal of the Korean Physical Society, Vol. 66, No. 7, April 2015, pp. 1039∼1044

Transient Photocurrent Responses in Amorphous Zn-Sn-O Thin Films

Ju-Yeon Kim, Sang-A Oh, Kyeong Min Yu and Byung Seong Bae
Department of Display Engineering, Hoseo University, Asan 336-795, Korea

Eui-Jung Yun*
Department of Information and Communication Engineering, Hoseo University, Asan 336-795, Korea

(Received 28 April 2014, in final form 12 January 2015)

In this study we characterized the transient photocurrent responses in solution-processed amorphous zinc-tin-oxide (a-ZTO) thin films measured under light illumination with a wavelength of 400 nm at different temperatures. By using the temperature-dependent photoconductivities of a-ZTO thin films, we extracted the activation energies (E_{ac}) of photo-excitation and dark relaxation through an extended stretched exponential analysis (SEA). The SEA was found to describe well the dark relaxation characteristics as well as the photo-excitation processes. The SEA also indicates that the dark relaxation process reveals a dispersive transient photoconductivity with a broader distribution of the E_{ac} while the photo-excitation process shows non-dispersive characteristics. Samples exposed by light at temperatures less than 373 K possess the fast processes of photo-excitation and dark relaxation. This suggests that a fast process, for example, a generation/recombination of charged carriers related to a band-to-band transition and/or shallow/deep oxygen-vacancy (V_o) sub-gap donor states, is dominant in the case of light illumination at low temperatures of less than 373 K. The SEA indicates, however, that a much slower process due mainly to the delay of the onset of ionization/neutralization of the deep V_o states by multiple-trapping is dominant for samples under light illumination at a high temperature of 373 K. Based on the experimental results, for the dark relaxation process, we conclude that the process transitions from a fast recombination of electrons through band-to-band transitions and/or shallow/deep V_o donor states to a slow neutralization of the ionized V_o states occurs due to enhanced carrier multiple-trapping by relatively deep V_o trap states when the temperature becomes greater than 363 K. An energy band diagram of a-ZTO thin films was proposed in terms of the temperature and the E_{ac} distribution to explain these observed results.

PACS numbers: 73.50.Gr, 73.50.Pz, 73.61.Jc, 73.25.+i
Keywords: Transient photocurrent responses, Solution-processed amorphous zinc-tin-oxide, Stretched exponential analysis
DOI: 10.3938/jkps.66.1039

I. INTRODUCTION

Solution-deposited amorphous Zn-Sn-O (a-ZTO) thin films deposited by using spin coating, dip coating, or inkjet printing have been intensively utilized as a channel material for thin film transistors (TFTs) in flat panel displays owing to their high field-effect mobility of up to 25 cm^2/Vs, simplicity, low-cost, high throughput, and non-toxicity [1–5]. The properties of amorphous oxide TFT, however, are very sensitive to exposure to light and/or temperature and it is of great importance for a-ZTO TFTs to exhibit illumination stress (IS)-independent stabilities, so the stability of oxide TFTs under the applications of IS has recently become an important issue [6–11].

The research on single a-ZTO thin films is very limited and is based mainly on the study of a-ZTO TFTs which have a complex structure due to the presence of the gate insulator/semiconductor interface. We can also utilize the transient photoconductivity characteristics to design new optoelectronic devices [12]. Thus, these characteristics in a-ZTO thin films should be more carefully characterized.

Stretched exponential fits have been successfully used to analyze the photoresponses in a-Si [13, 14] and a-In-Ga-Zn-O material systems [12]. However, there is, at present, no information in the literature on a study of the photoresponses in solution-processed a-ZTO thin films. Therefore, in this study, we report the transient photocurrent responses in solution-processed a-ZTO thin films measured under light illumination at a wavelength (λ) of 400 nm at different temperatures.

*E-mail: ejyun@hoseo.edu; Tel: +82-41-5405675; Fax: +82-41-5405587

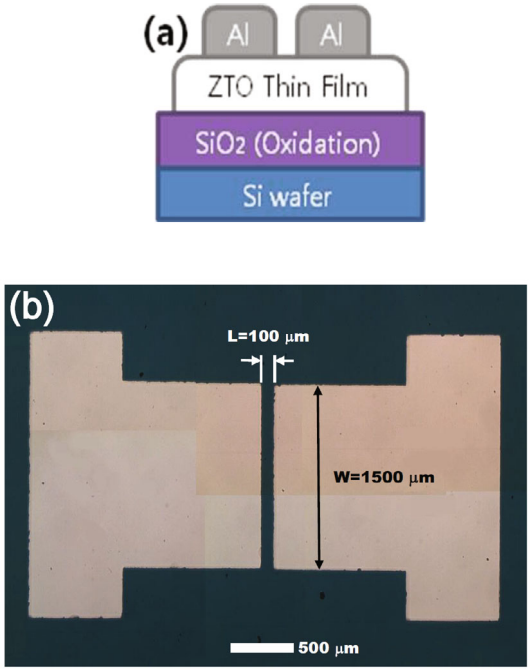

Fig. 1. (Color online) (a) Schematic cross-sectional view and (b) photographic top view of samples developed in this work: W = 1500 μm and L = 100 μm.

II. EXPERIMENTS

The fabrication process of samples is as follows: The precursor solution for the ZTO active layer was synthesized using a sol-gel method by dissolving zinc-acetate-dehydrate and tin-chloride powders in 2-methoxyethanol, which was stabilized by using acetyl acetone. The concentration of the precursor solution was 0.3 M with a Zn/Sn molar ratio of 1. The precursor solution was stirred for 8 hrs at 353 K, filtered through a 0.2-μm membrane syringe filter, and spin-coated at 5000 rpm for 50 sec on the top of a 300-nm-thick SiO_2 dielectric layer that had been thermally grown on a Si wafer. Then, a ZTO prebake process was carried out at 373 K for 1.5 min on a hot plate in air to evaporate the solvent. The precursor film was then converted to a 40-nm-thick ZTO thin film by annealing at 873 K for 1 hr in a furnace. To prepare two patterned electrodes on the top of ZTO thin films, we deposited a 100-nm-thick aluminum (Al) layer through a shadow mask by using a thermal evaporator at a pressure of 10^{-6} Torr. Figures 1(a) and 1(b) show a schematic cross-sectional view and a photographic top view, respectively, of typical samples prepared in this study. The width (W) and the length (L) of the samples were 1500 μm and 100 μm, respectively.

The transient photocurrent responses of the solution-processed a-ZTO thin films were measured under light illumination with a wavelength of 400 nm at different temperatures in the range of 333 − 373 K. To avoid the effect of moisture and other impurities, we conducted the measurements in a vacuum chamber. The photocurrent measurements were also performed with a voltage of 3 V by using two Keithley 2400 source meters for a DC voltage source and a Keithley 6485 picoammeter for current measurements. For the measurements of the transient photocurrent characteristics, a LED light source with a λ of 400 nm was used at a constant photon flux (N_{ph}) of 1.83 × 10^{17} photons/cm^{2}s. The illumination duration was one hour.

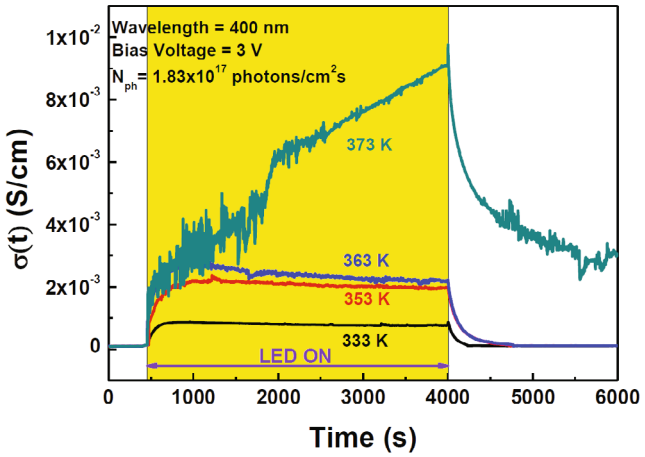

Fig. 2. (Color online) Comparison of photo-excitation and dark relaxation conductivities as functions of time at various temperatures for solution-processed a-ZTO thin films under light illumination with a wavelength of 400 nm and a photon flux (N_{ph}) of 1.83 × 10^{17} photons/s·cm^2.

III. RESULTS AND DISCUSSION

Figure 2 shows the typical conductivities (σ(t)) versus time (t) characteristics as a function of temperature for solution-processed a-ZTO thin films under light illumination with a λ of 400 nm and a N_{ph} of 1.83 × 10^{17} photons/s·cm^2. The conductivity of an a-ZTO thin film at time t, σ(t), which describes the photo-excitation and the dark relaxation processes, was estimated using the following equation [15]:

$$\sigma(t) = \frac{L}{W t_c V_{app}} I(t), \quad (1)$$

where L, W, and t_c are the length, width, and thickness of the a-ZTO thin film, respectively, V_{app} is the applied voltage, and $I(t)$ is the current measured at t. As shown in Fig. 2, for samples exposed to light with a λ of 400 nm and a N_{ph} of 1.83 × 10^{17} photons/s·cm^2 at temperatures less than 373 K, the sample conductivity saturated rapidly after the LED had been turned on while it recovered its initial value shortly after the LED had been turned off, indicating the presence of fast photo-induced processes with short time constants in the

photoconductivity response of the samples measured at temperatures less than 373 K. It is also worth noting that the magnitude of the photoconductivity increases with increasing measurement temperature up to 363 K at a constant photon flux illumination and then decreases back to its original value shortly after the constant flux of light is removed. This implies that the increase in the photo-induced carrier density is accelerated by temperature. We believe that these fast processes are attributed to a generation/recombination of electron-hole pairs related to band-to-band and/or deep defect donor states because the energy (3.1 eV) corresponding to a 400-nm wavelength is comparable to the band gap of a-ZTO.

On the other hand, the sample conductivity was still changing continuously, but at significantly slower rates, for samples measured at a high temperature of 373 K. On the basis of many research results reported in the recent literature [8,12,16], the slow increase and slow decrease in the photoconductivity can be related to an increase and a decrease in the donor carrier density due mainly to the photoionization of oxygen vacancy (V_o) states and the neutralization of ionized V_o (V_o^{2+}), respectively.

A stretched exponential analysis (SEA) was employed to deduce the time constant distribution and corresponding activation energy distribution related to the result shown in Fig. 2. The photoconductivity change over time t, σ_{ph}(t), which follows the stretched exponential function, can be described by using the equation [12]

$$\sigma_{ph}(t) = |\sigma(t) - \sigma_S| = \sigma_0 e^{-(t/\tau)^{\beta}}, \quad (2)$$

where σ_{ph}(t) is the difference between the time-dependent conductivity expressed in Eq. (1) and the asymptotic conductivity σ_s at long times, σ_0 is the weighing amplitude, τ is the effective time constant, and β is the stretching exponent. σ_s is either the saturation conductivity for the photo-excitation process or the relaxed dark conductivity for the dark relaxation process. τ can be defined as the time when the σ_{ph}(t) relaxes to 1/e of σ_0 and is related to a thermally-activated process with activation energy E_{ac} [17]:

$$\tau = \frac{1}{f} e^{E_{ac}/k_B T}, \quad (3)$$

where f is the attempt-to-escape frequency, assumed to be 10^{13} Hz [8,17], k_B is Boltzmann's constant, and T is the sample temperature. From τ and Eq. (3), we can calculate the E_{ac} values that characterize the transient photocurrent response shown in Fig. 2. Furthermore, the bandwidth of the E_{ac} (BW_{ac}), which is defined as the full width at half maximum of the distribution of the E_{ac}, can be estimated by making use of the equation

$$BW_{ac} = 4.6(\beta^{-0.81} - 1)k_B T. \quad (4)$$

Equation (4) is a simple empirical equation derived by other research groups [12, 17], and fits the estimated BW_{ac} to within 8%, provides a simple way to calculate the BW_{ac} for any β in the range $0.05 < \beta < 1$, and indicates the increase in BW_{ac} with decreasing β.

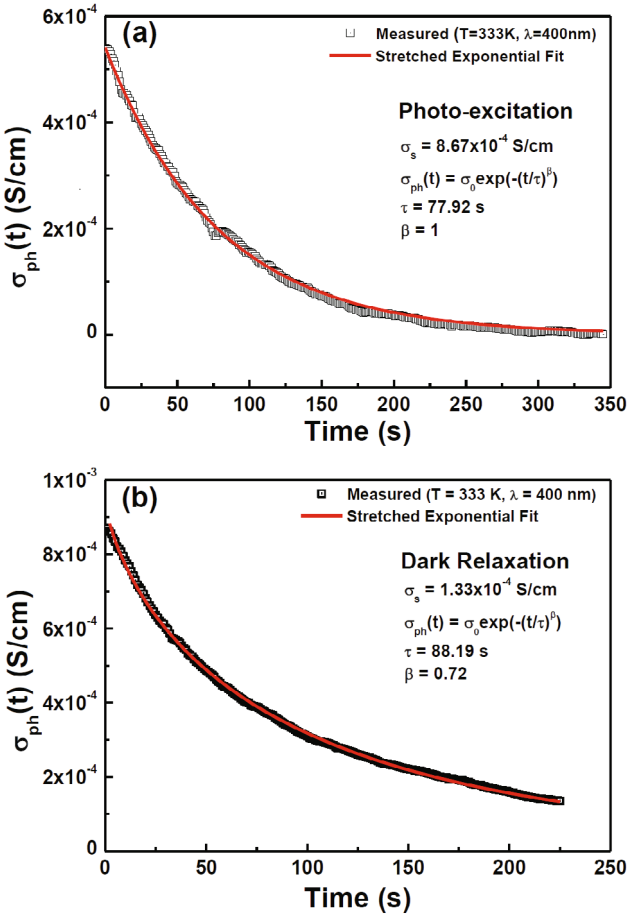

Fig. 3. (Color online) One typical example of best stretched exponential fits to the photoconductivity data for 333 K shown in Fig. 2: (a) photo-excitation process and (b) dark relaxation process. The solid lines in (a) and (b) show the fitted curves, which were obtained from the stretched exponential analysis by making use of Eq. (2).

We extracted important fitting parameters, such as τ, E_{ac}, β, and BW_{ac}, by using Eqs. (1) – (4), and these parameters obtained from the results in Fig. 2 are summarized in Table 1. Figures 3 and 4 show typical examples of a best stretched exponential fits to the photoconductivity data shown in Fig. 2 for a-ZTO thin films at 333 K and 373 K, respectively, and demonstrate that the stretched exponential function provides an excellent fit. The temperature dependence of the stretched fitting parameters for the photo-excitation and the dark relaxation processes in solution-processed a-ZTO thin films under light illumination at different temperatures, which are obtained from the results in Fig. 2 and Table 1, is illustrated in Fig. 5. As shown in Fig. 5, a-ZTO thin films exposed to a constant photon flux at temperatures less than 373 K possess much shorter τ and smaller E_{ac} (by around 150 meV) compared to those exposed to the

Table 1. Summary of important fitting parameters deduced from the characteristics shown in Fig. 2 by making use of Eqs. (1) – (4).

Stress Condition	Photo-excitation Parameters					Dark Relaxation Parameters				
	τ (s)	E_{ac} (eV)	β	BW_{ac} (eV)	σ_s (S/cm)	τ (s)	E_{ac} (eV)	β	BW_{ac} (eV)	σ_s (S/cm)
λ = 400 nm, T = 333 K	78	0.98	1	0	8.7×10^{-4}	88	0.99	0.72	0.04	1.3×10^{-4}
λ = 400 nm, T = 353 K	142	1.06	0.93	8×10^{-3}	2.2×10^{-3}	122	1.05	0.63	0.06	1.4×10^{-4}
λ = 400 nm, T = 363 K	116	1.09	0.97	3×10^{-3}	2.7×10^{-3}	104	1.08	0.58	0.07	1.4×10^{-4}
λ = 400 nm, T = 373 K	1118	1.19	1	0	9.1×10^{-3}	480	1.16	0.29	0.23	1.4×10^{-4}

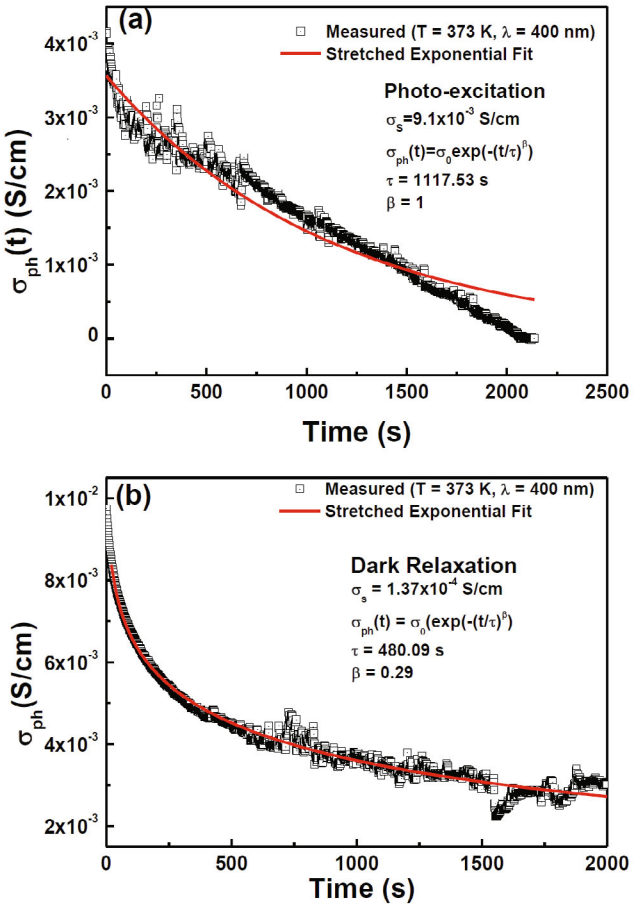

Fig. 4. (Color online) One typical example of best stretched exponential fits to the photoconductivity data for 373 K shown in Fig. 2: (a) photo-excitation process and (b) dark relaxation process. The solid lines in (a) and (b) show the fitted curves, which were obtained from the stretched exponential analysis by making use of Eq. (2).

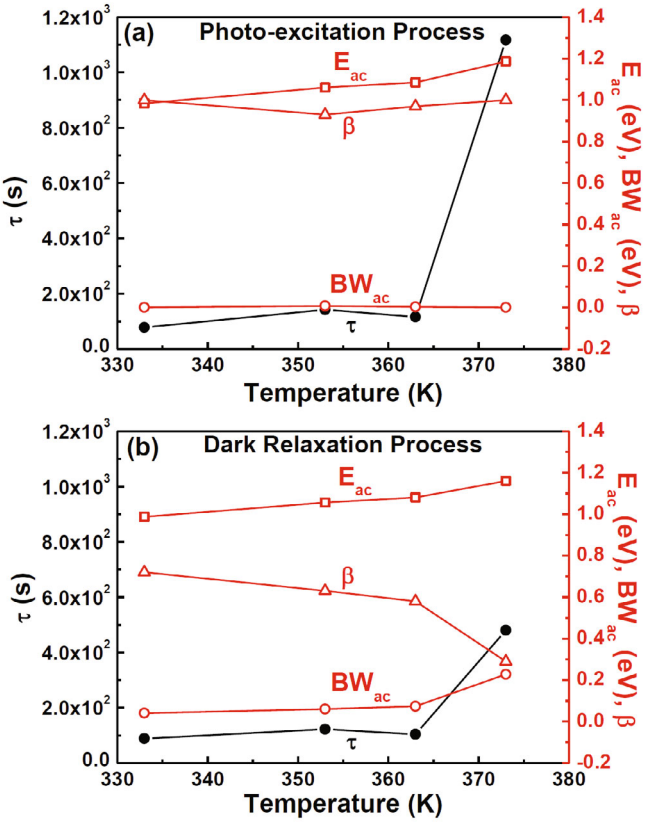

Fig. 5. (Color online) Temperature-dependences of the stretched fitting parameters for (a) the photo-excitation process and (b) the dark relaxation process in solution-processed a-ZTO thin films under light illumination at different temperatures, which were obtained from the results in Fig. 2 and Table 1.

same constant flux at a high temperature of 373 K for both photo-excitation and dark relaxation. The kinetics of transient photocurrents in amorphous semiconductor thin films are known to depend strongly on temperature and to be governed by the multiple-trapping model whereby the energy distribution (BW_{ac}) of the deep trap states located below the E_{ac} plays a key role [18]. Therefore, the above results support the conclusion that a fast process of generation/recombination of electron-hole pairs (EHPs) related to shallower defect centers located below E_{ac} and/or a band-to-band transition is dominant for photo-excitation and dark relaxation in the case of low temperatures less than 373 K.

As can be seen in Fig. 5, in the case of a high temperature of 373 K, however, the kinetics of the photoconductivity rise and decay for the samples have much longer τ and much larger E_{ac} than those corresponding to the case of low temperatures less than 373 K, suggesting that much slower processes are involved and much deeper trap states located below the 1.2-eV E_{ac} level play an important role in the photo-excitation and the dark relaxation kinetics of samples measured at 373 K. Recent research [8,12,16,19] has reported that amorphous-oxide semiconductors such as a-ZTO and a-IGZO have deep sub-gap states located below 1.2 eV from the conduction band edge, which are attributed to V_o states. Thus, we conclude that the ionization and the neutralization of V_o states are main mechanisms for both the photo-excitation and the dark relaxation kinetics of samples measured at 373 K.

For the dark relaxation process shown in Fig. 5(b), the β decreases slowly and the BW_{ac}, the τ, and the E_{ac} increase slightly with increasing temperature up to 363 K while the decrease in β and the increases in BW_{ac}, τ, and E_{ac} tend to be more severe at a higher temperature of 373 K. These phenomena for a high temperature of 373 K can be explained in term of the multiple-trapping model [18] as follows: Multiple trapping of charge carriers by deep sub-gap states located below the E_{ac} (which is also called the demarcation energy) tends to be enhanced for a high temperature of 373 K, which, in turn, leads to dispersive transient photoconductivity with a much lower β and a much wider BW_{ac}, delays the onset of charge carrier recombination, and causes a slower photoconductivity decay with a much longer lifetime τ. A recent study [20] reported that the V_o in solution-processed a-ZTO films could cause deep levels as well as shallow levels, depending on its local structure, and can act as electron trap centers in deep states instead of recombination centers. Furthermore, trapping centers located deep in the band gap are well-known [21] to be slower in releasing trapped carriers than are the centers located near the conduction band. This results from the fact that more energy is required to reexcite a trapped electron from a center near the deep gap states to the conduction band than is required to reexcite an electron from a center closer to the conduction band. These facts confirm that the multiple trapping of electrons by deep sub-gap V_o states located below the E_{ac} controls the kinetics of transient photoconductivity decay for samples measured at a temperature of 373 K. Thus, for the dark relaxation process, we conclude that the process transition from a fast recombination of electrons through band-to-band transitions and/or shallow/deep V_o donor states to a slow neutralization of the ionized V_o states occurs due to enhanced carrier multiple-trapping by relatively deep V_o trap states when the temperature becomes greater than 363 K. These results may be effectively accounted for by considering the energy band diagrams of a-ZTO thin films at two different temperatures of 333 and 373 K depicted in Fig. 6.

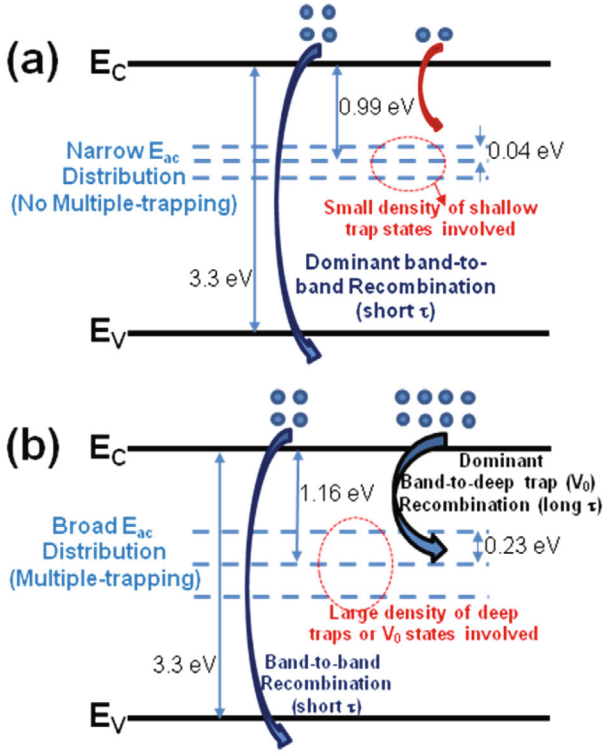

Fig. 6. (Color online) Suggested energy band diagrams for a-ZTO thin films at two different temperatures, (a) 333 K and (b) 373 K, to explain the experimental results for the dark relaxation process shown in Fig. 5 (b).

However, as shown in Fig. 5(a), a constant β (near unity) and a much narrower BW_{ac} (close to zero) were observed for the photo-excitation process compared to those for the dark relaxation process shown in Fig. 5(b). This suggests that non-dispersive transport is dominant in the kinetics of the transient photoconductivity rise.

IV. CONCLUSION

In this study, we investigated the transient photocurrent responses in solution-processed a-ZTO thin films measured under light illumination with a wavelength of 400 nm at different temperatures. On the basis of the experimental results extracted from the extended stretched exponential analysis, we conclude that the kinetics of transient photocurrents in a-ZTO thin films are found to depend strongly on the temperature and to be governed by the multiple-trapping model. For the dark relaxation process, we conclude that a process transition from a fast recombination of electrons through band-to-band transitions and/or shallow/deep V_o donor states to a slow neutralization of the ionized V_o states occurs due to enhanced carrier multiple-trapping by relatively deep V_o trap states when the temperature becomes greater than

363 K. We also conclude that non-dispersive transport is dominant for the kinetics of transient photoconductivity rise whereas the kinetics of the transient photoconductivity decay reveals a dispersive transient photoconductivity with a broader distribution of the E_{ac}.

ACKNOWLEDGMENTS

This work was supported by the Industrial Strategic Technology Development Program (10041596, Development of core technology for TFT free active matrix addressing colour electronic paper with day and night usage), funded by the Ministry of Trade, Industry & Energy (MI, Korea).

REFERENCES

[1] C. G. Kim, N-H. Lee, Y-K. Kwon and B. Kang, Thin Solid Films **544**, 129 (2013).
[2] C-G. Lee and A. Dodabalapur, Appl. Phys. Lett. **96**, 243501 (2010).
[3] Y. B. Yoo, J. H. Park, S. J. Lee, K. M. Song and H. K. Baik, Jpn. J. Appl. Phys. **51**, 040201 (2012).
[4] Y. H. Hwang, S-J. Seo, J-H. Jeon and B-S. Bae, Electrochem. Solid-State Lett. **15**, H91 (2012).
[5] H. B. Kim and H. S. Lee, Thin Solid Films **550**, 504 (2014).
[6] K. H. Ji *et al.*, Appl. Phys. Lett. **98**, 103509 (2011).
[7] H. Oh, S-H. Ko Park, C-S. Hwang, S. Yang and M. K. Ryu, Appl. Phys. Lett. **99**, 022105 (2011).
[8] H. Oh, S-M. Yoon, M. K. Ryu, C-S. Hwang, S. Yang and S-H. Ko Park, Appl. Phys. Lett. **97**, 183502 (2010).
[9] S-H. Ko Park, M. Ryu, S. Yang, S. M. Yoon and C-S. Hwang, J. Information Display **11**, 113 (2010).
[10] T. Kamiya, K. Nomura and H. Hosono. Technol. Adv. Mater. **11**, 044305 (2010).
[11] B. Ryu, H-K. Noh, E-A. Choi and K. J. Chang. Appl. Phys. Lett. **97**, 022108 (2010).
[12] J. Luo, A. U. Adler, T. O. Mason, D. B. Duchholz, R. P. H. Chang and M. Grayson, J. Appl. Phys. **113**, 153709 (2013).
[13] D. Redfield and R. H. Bube, *Photoinduced Defects in Semiconductors* (Cambridge University Press, New York, 1996).
[14] R. H. Bube, L. Echeverria and D. Redfield, Appl. Phys. Lett. **57**, 79 (1990).
[15] J. H. Chung, J. Y. Lee, H. S. Kim, N. W. Jang and J. H. Kim, Thin Solid Films **516**, 5597 (2008).
[16] S-H. Ko Park, M. Ryu, S. M. Yoon, S. Yang, C-S. Hwang, J-H. Jeon and K. Kim, Jpn. J. Appl. Phys. **50**, 03CB08-1 (2011).
[17] D. H. Lee, K-I. Kawamura, K. Nomura, T. Kamiya and H. Hosono, Electrochem. Solid-state Lett. **13**, H324 (2010).
[18] M. S. Iovu, S. D. Shutov, V. I. Arkhipov and G. J. Adriaenssens, J. Non-Crystalline Solids **299-302**, 1008 (2002).
[19] T. Kamiya, K. Nomura and H. Hosono, J. Display Technol. **5**, 468 (2009).
[20] S-J. Seo, Y. H. Hwang and B-S. Bae, Electrochem. Solid-state Lett. **13**, H357 (2010).
[21] B. G. Streetman and S. K. Banerjee, *Solid State Electronic Devices*, 6th ed. (Pearson Prentice Hall, Upper Saddle River, NJ, 2006).