

Influence of fluorine doping on spin-coated indium gallium zinc oxide (IGZO) thin film properties

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Amorphous Indium Gallium Zn-O (a-IGZO) is the most suitable channel material for thin-film transistors (TFTs). In this work, Fluorine (F) doped a-IGZO thin films were deposited on glass substrates using a facile spin-coating sol gel method. The effect of F doping on the structure, electrical and optical properties was investigated. X-ray diffraction (XRD) characterization shows that all deposited IGZO thin films have an amorphous structure and scanning electron microscope (SEM) showed smooth surfaces for all films. Resistivity measurement indicated that F doping systematically decreases the film sheet resistance to achieve $65 \Omega/cm^2$ while optical characterization show that the deposited thin films transmittance is slightly enhanced to about 85%. Energy-dispersive X-ray spectroscopy (EDS) and photoluminescence spectroscopy (PL) show that F-doping affects the Oxygen vacancy. This latter decreases with increasing F doping. These findings indicate that doping by Fluorine can be a key factor for developing low cost and high performance IGZO TFTs.

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1. Introduction

Amorphous Indium Gallium Zinc Oxide semiconductors (a-IGZOs) have been extensively studied as the active layers in thin-film transistors (TFTs) [1] and materials for Display and Memory [2,3]. a-IGZOs have many advantages such as high mobility, optical transparency, and the possibility of low temperature processing on flexible substrates [4,5]. a-IGZOs are widely used to fabricate the active channel layer in TFTs since the amorphous-state is attractive for large-area uniformity [6]. Solution processes has been developed due to the possibility of next-generation techniques for the low-cost fabrication of large-areas without using vacuum deposition techniques although thin films deposited by low-cost methods have poor properties compared to vacuum methods [7–9]. One of the major problems of a-IGZO thin films and devices is its instability under different types of optical and electrical stresses which may induce rigid negative threshold-voltage shift, as well as a subthreshold hump and an increase in subthreshold-voltage slope and this is mainly due oxygen vacancy states (V_O) [10,11] and hence traps [12–14]. Several works aimed to improve the quality of a-IGZO thin films mainly by doping with metals and other elements [15–17] or by other methods [18–21]. Hydrogen is the most common external dopant of amorphous oxide semiconductors (AOSs) and a-IGZO thin films and devices, and has a great influence on the performance of thin-film transistors (TFTs) based on these materials [22,23]. Nitrogen is also known to influence the properties of a-IGZO thin films and devices and stabilizes a-IGZO based TFTs under ambient operation conditions [24–29]. To improve the

bias-induced instability of a-IGZO TFTs, Sanghyun Cho et al. doped a-IGZO TFT thin films channel using yttrium [30]. The electrical properties of IGZO TFTs such as mobility, subthreshold swing and on/off ratio are improved by Mg doping that can also stabilize device performance under positive gate bias or negative gate bias with illumination stress [31]. Incorporation of Fluorine in IGZO thin films shows improvement in their properties and hence in the device performance [32–34]. However, few works were reported using sol gel-based growth methods. In this work we study the influence of Fluorine on the electrical, optical and structural properties of a-IGZO thin films deposited by the low-cost sol-gel spin coating on a glass substrate.

2. Materials and methods

The InGaZnO (IGZO) precursor solution was prepared by dissolving indium (III) acetate hydrate ($\text{In}(\text{NO}_3)_3 \cdot \text{H}_2\text{O}$ 99.99% Alfa easer), gallium(III) nitrate hydrate ($\text{Ga}(\text{NO}_3)_3 \cdot \text{H}_2\text{O}$ 99.99% Sigma-Aldrich), and zinc acetate dehydrate ($\text{Zn}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$ 99.99% Sigma-Aldrich), 2-methoxyethanol (2-ME) solvent, and then ethanolamine (MEA). Acetylacetone (Acac) was added to the mixed solution as sol-stabilizers to improve the solubility of the solution. The resultant solution was stirred at 60 °C for 2 h to yield a clear and transparent precursor solution. The molar ratio of In:Ga:Zn was maintained at 2:1:1 and the total concentration of metal ions in the resultant solution was 0.3 M. The as-synthesized precursor solution was aged for 24h to increase the partial homogenization of the solution before it was used as the

coating solution. For Fluorine doping, Ammonium Fluoride (NH_4F 98%, Alfa aesar) was solved in ethanol and is added to IGZO solution by ratios of 2%, 4% and 6%. The solution was deposited on a commercial glass by spin-coating (holmarc Ho-th-05) at a rotation speed of 3000 rpm for 30 s. The liquid film was dried at 150°C on a hot plate for 10 min to evaporate organic compounds. The whole procedure was then repeated for 5 times. The dried film was then annealed in oven at 350°C for 2 h. Fig. 1 shows a schematic illustration of the deposition process of a-IGZO thin films by spin coating.

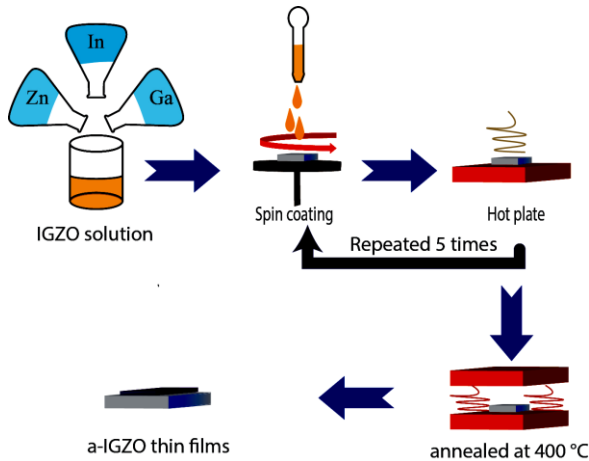


Fig. 1. Schematic illustration of the deposition process to prepare IGZO thin films by the sol gel spin coating method (color online)

3. Results and discussion

The obtained films for different ratio of F were characterized by the four-point probe method to measure their sheet resistance and the results are shown in Fig. 2. F-doping clearly has a significant impact on enhancing the electrical properties. The sheet resistance is reduced by as much as 50% for a 6% F-doping. This result is important, since good conductivity is required for IGZO TFT channel, for example. The increased conductivity is probably due to oxygen vacancy defect reduction since it is a well-known fact that Oxygen vacancy, in TCOs, is the major player for determining the thin film conductivity and usually reduced by doping since the dopant species usually occupies Oxygen vacancies as mentioned in the introduction section.

It is worth noting that after the incorporation of F, we expect the Hall mobility and electron concentration to improve significantly. Consequently, conductivity increases with the increasing concentration of F doping. Similar results were found in other works about Zinc Oxide [35,36]

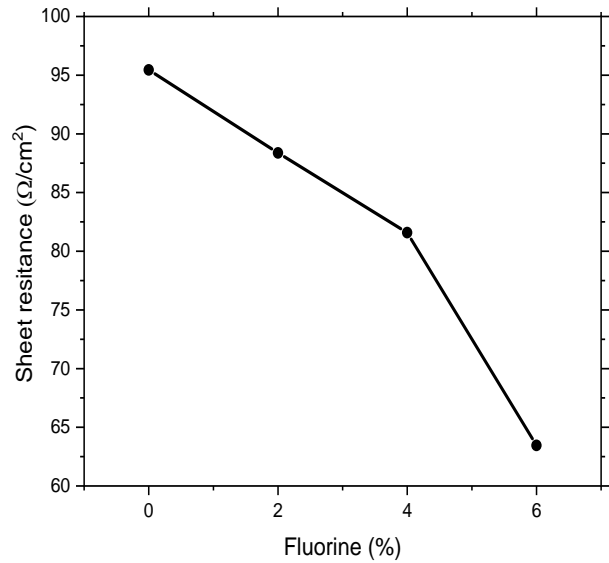


Fig. 2. Variation of sheet resistance various fluorine doping

For the structural characterization, Fig. 3 shows XRD results of annealed IGZO thin films. These diffraction patterns were examined using a thin film X-ray diffractometer using $\text{CuK}\alpha$ radiation ($\lambda 1.5406 \text{ \AA}$) with a glancing incident angle of 0.8° . No observable diffraction peaks were detected from these thin films. However, each pattern showed a weak and broad diffraction signal in the 2θ range of $20\text{--}90$ degree. Such a feature indicated that the structure of thin films have an amorphous phase.

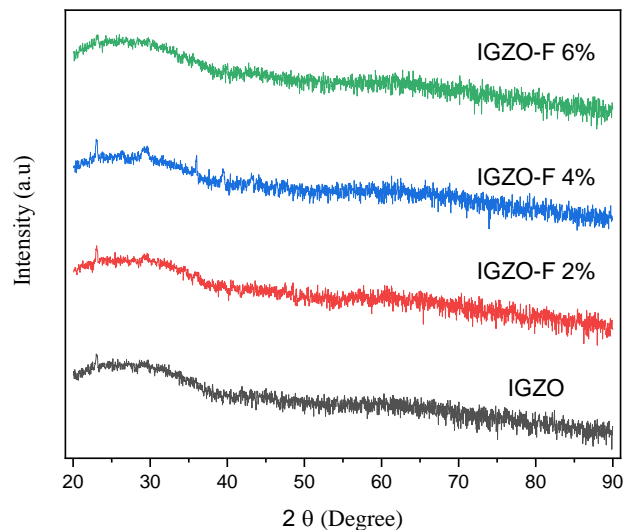


Fig. 3. XRD patterns of the sol-gel derived IGZO thin films annealed at various fluorine percentage (color online)

An SEM image of the different F-doped IGZO film is shown in Fig. 4. An amorphous phase with no prominent crystalline phase can be observed with a smooth surface.

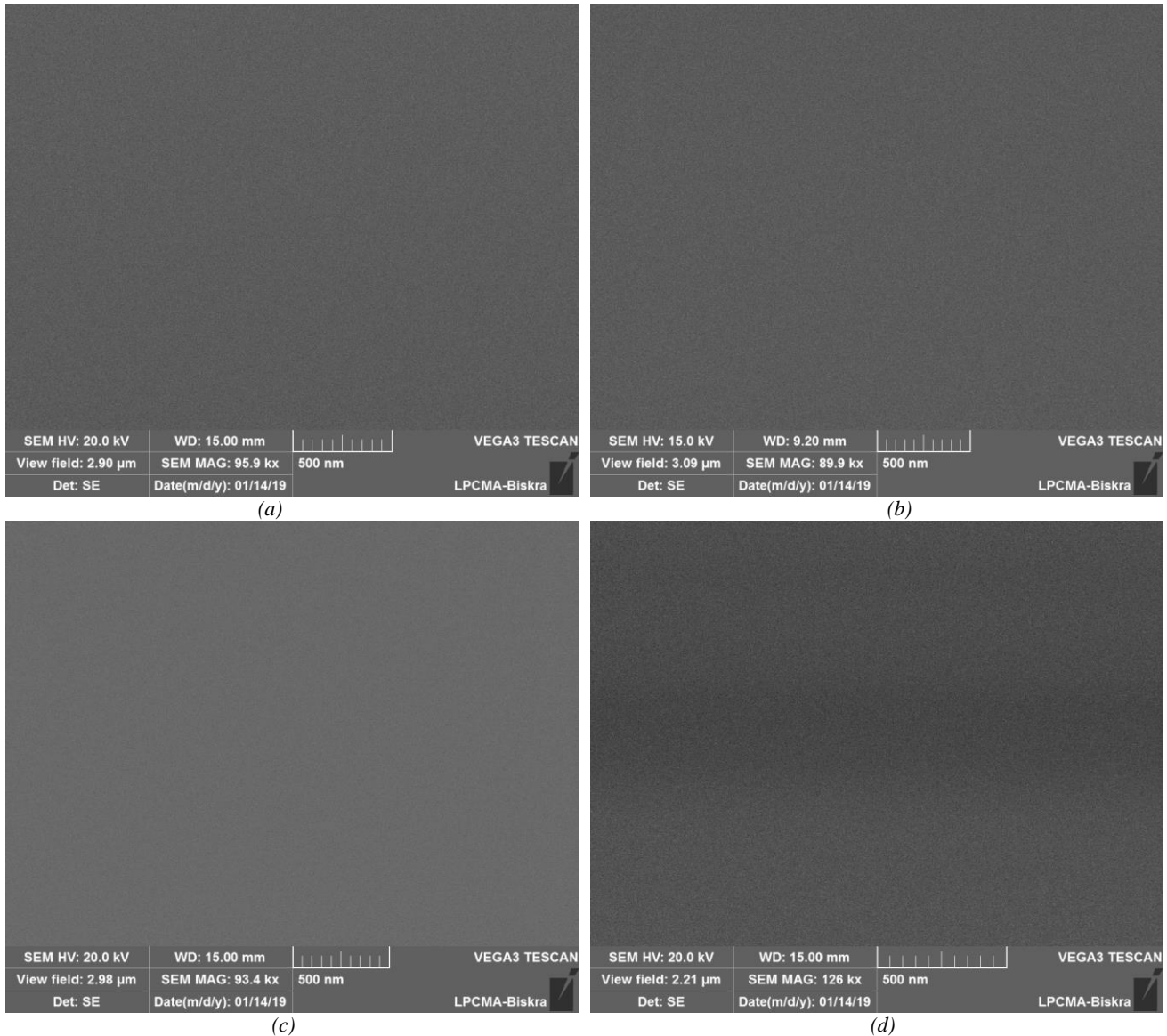


Fig. 4. SEM photo images a) undoped IGZO b) IGZO-F2% c) IGZO-F4% d) IGZO-F6%

The IGZO thin film composition is observed by EDS, as shown in Table 1. The IGZO thin film composition is very similar to the solution composition. F-doping increases Oxygen, which decreases the Oxygen vacancy, while it reduces Indium. This may be the cause for the observed increase of the conductivity of the thin films by F-doping.

Table 1. IGZO thin film composition by EDS

	In	Ga	Zn	O	F
IGZO	28.1	12.8	12.4	46.50	0
IGZO-2%	27.5	12.5	12.7	50.3	0.7
IGZO-4%	22.3	12.6	11.5	52.3	1.3
IGZO-6%	17.6	12.3	11.6	56.0	2.5

The optical characterization was first a baseline measurement of the original substrate transmittance was obtained using an ultraviolet–visible (UV–Vis) spectrophotometer and then the grown a-IGZO thin films. The transmittance of these films is presented in Fig. 5 for the different F ratios. The prepared films had high average transmittance values (over 85%) in the visible region, as shown. The obtained results show similarity with other works [37–39]

The absorption edge does not show any variation with Fluorine doping. This reveals that the F doping does not influence the band gap (E_g), of IGZO. E_g was estimated by calculating the absorption coefficient using

$$\alpha = (1/t)\ln[1/T]$$

where t is the film thickness and T is the transmittance. The optical bandgap was calculated using the Tauc relationship ($(\alpha h\nu)^2$ vs. $h\nu$), as shown in Fig. 6.

F does not affect the band structure because it is, atomically, smaller than other elements. Therefore, its outer shells do not contribute to the conduction and perhaps the valence band of the material.

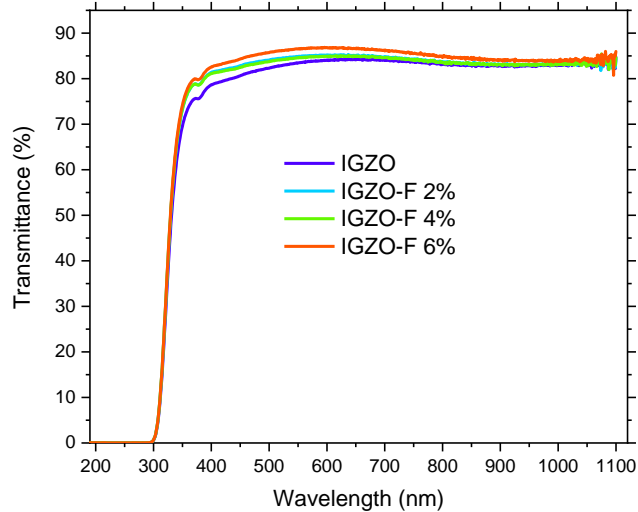


Fig. 5. Optical transmittance spectra of glass substrate and glass/a-IGZO thin film samples (color online)

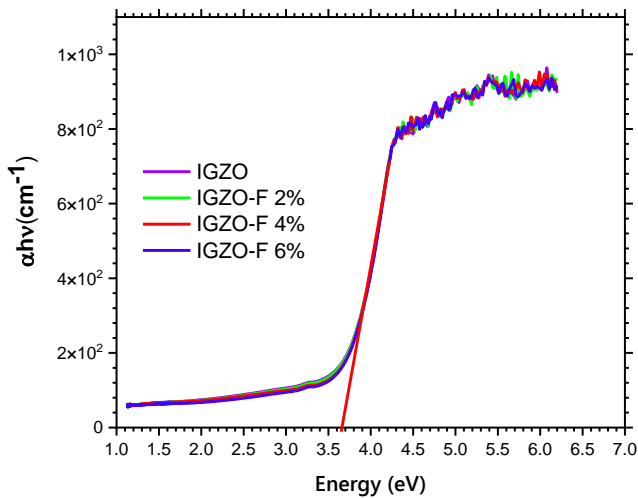


Fig. 6 The plot of $(\alpha h\nu)^2$ vs. photon energy $(h\nu)$ of the IGZO thin films (color online)

Fig. 7 shows the reflection results in the same wavelength range. In the visible light region, the reflection is strongly affected by the thin film topography, including the surface roughness and the size and pattern of surface asperities. In this wavelength range, the results in Fig. 5 indicate that surface roughness becomes the dominant factor of reflection; the specimen with a larger roughness value has a higher reflection as the result. Doping by Fluorine reduces this reflectance and hence enhances transmission and therefore absorption.

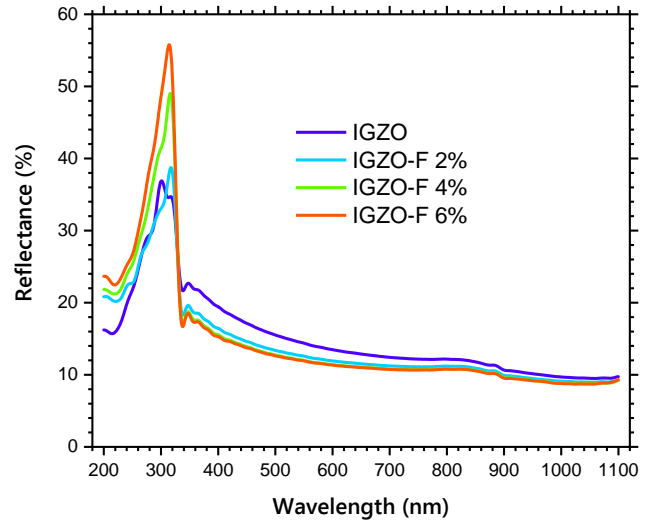


Fig. 7. Reflectance spectra of a-IGZO thin film samples (color online)

In order to confirm the reduction of oxygen related defect sites in the F doped IGZO thin films, room temperature PL spectra are shown in Fig. 8. All thin films showed the strongest luminescence peak at 440 nm, indicating near-band-edge transition. There is a wide emission band at around 550 nm region, which represents the green emission in the visible light region. This emission represents oxygen vacancies and interstitial Zn in ZnO [40]. Thus, a decrease in the intensity in the visible light region at around 550 nm indicates that oxygen vacancies are filled due to F doping. The green emission decreases as the F amount increases in IGZO thin films which may be due to deep defects in the band gap.

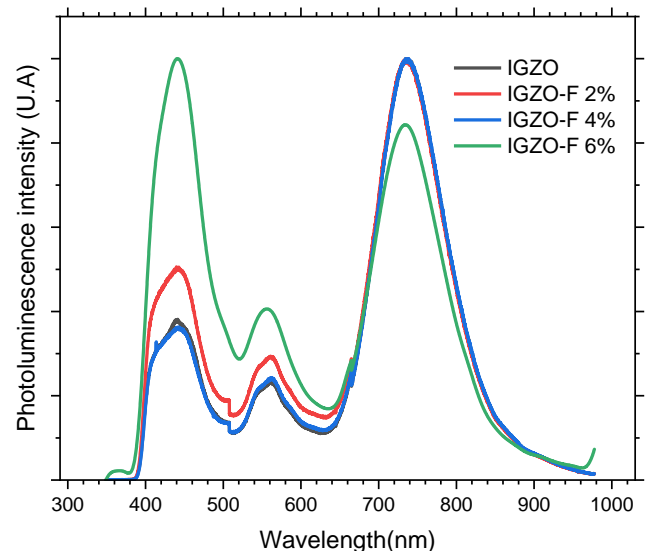


Fig. 8. PL spectra of pure IGZO, IGZO-F2%, IGZO-F4% and IGZO-F6% films at room temperature (color online)

4. Conclusion

Fluorine-doped a-IGZO thin films were successfully prepared on glass substrates by a facile cost-effective sol-

gel spin coating method. The structural, optical and electrical properties of these F doped a-IGZO films have been thoroughly investigated. X-ray diffraction (XRD) characterization revealed an amorphous structure for all deposited IGZO thin films. These films had smooth surfaces characterized by a scanning electron microscope (SEM). Thin films of IGZO:F with 6% F exhibit the lowest sheet resistance, which is promising for application in low-cost devices. IGZO films show high transmittance of about 85% and low reflectance in the visible region. Transmittance is slightly enhanced by F doping in the visible spectrum. Energy-dispersive X-ray spectroscopy (EDS) revealed that F-doping greatly increases Oxygen and reduces Indium, while it has minor effect on Gallium and Zinc composition in the prepared a-IGZO thin films which indicate that effectively Oxygen vacancies are reduced. Furthermore, photoluminescence spectroscopy (PL) showed near-band-edge transition in all a-IGZO films and a wide emission band at around 550 nm region, which represents the green emission in the visible light region. This latter decreases with increasing F doping. All these combined results indicated that Oxygen vacancy has decreased with F doping increase and hence the defects which led to the thin films properties enhancement. These findings indicate that doping by Fluorine may be very useful in developing low cost with high-performance devices base on a-IGZO thin films.

References

- [1] H. Kumomi, *Amorphous Oxide Semiconductors: IGZO and Related Materials for Display and Memory*, John Wiley and Sons Ltd, Chichester, 21 (2022).
- [2] H. Hosono, *Amorphous Oxide Semiconductors: IGZO and Related Materials for Display and Memory*, John Wiley and Sons, Chichester, 1 (2022).
- [3] S. Yamazaki, T. Tsutsu, *Physics and Technology of Crystalline Oxide Semiconductor CAAC-IGZO: Application to Displays*, John Wiley and Sons Ltd., Chichester, 2017.
- [4] X. Yu, T.J. Marks, A. Facchetti, *Nat. Mater.* **15**, 383 (2016).
- [5] J. Troughton, D. Atkinson, *J. Mater. Chem. C Mater.* **7**, 12388 (2019).
- [6] N. Tiwari, A. Nirmal, M. R. Kulkarni, R. A. John, N. Mathews, *Inorg. Chem. Front.* **7**, 1822 (2020).
- [7] C. Kashif Tufail, *Thin Films*, Intech Open 2021.
- [8] M. Eslamian, *Nano-Micro Lett.* **9**, 3 (2017).
- [9] S. Ceron, O. Obregon, A. Orduña-Díaz, M. A. Dominguez, *Transactions on Electrical and Electronic Materials* **23**, 489 (2022).
- [10] M. Mativenga, F. Haque, M. M. Billah, J. G. Um, *Sci. Rep.* **11**, 14618 (2021).
- [11] H.-W. Yeon, S.-M. Lim, J.-K. Jung, H. Yoo, Y.-J. Lee, H.-Y. Kang, Y.-J. Park, M. Kim, Y.-C. Joo, *NPG Asia Mater* **8**, e250 (2016).
- [12] M. Benwadih, J.A. Chroboczek, G. Ghibauda, R. Coppard, D. Vuillaume, *J. Appl. Phys.* **115**(21), 214501 (2014).
- [13] W. Körner, D.F. Urban, C. Elsässer, *J. Appl. Phys.* **114**(16), 163704 (2013).
- [14] G. Li, A. Abliz, L. Xu, N. André, X. Liu, Y. Zeng, D. Flandre, L. Liao, *Appl. Phys. Lett.* **112**(25), 253504 (2018).
- [15] J. Seo, H. Yoo, *Micromachines* **12**, 481 (2021).
- [16] H. Yang, X. Zhou, H. Fu, B. Chang, Y. Min, H. Peng, L. Lu, S. Zhang, *ACS Appl. Mater. Interfaces* **13**, 11442 (2021).
- [17] S. Parthiban, J.-Y. Kwon, *J. Mater. Res.* **29**, 1585 (2014).
- [18] C. Chen, C. Liu, J. Zheng, G. Li, S. Li, Q. Wu, J. Wu, C. Liu, *Journal of Information Display* **20**, 161 (2019).
- [19] I. Kim, J. Yun, T. Badloe, H. Park, T. Seo, Y. Yang, J. Kim, Y. Chung, J. Rho, *Photonics Res.* **8**, 1409 (2020).
- [20] J. Kim, H. Hiramatsu, H. Hosono, T. Kamiya, *Journal of the Ceramic Society of Japan* **123**, 537 (2015).
- [21] J.-Y. Lee, K.-J. Heo, S.-G. Choi, H.G. Ryu, J.-H. Koh, S.-J. Kim, *Journal of Semiconductor Technology and Science* **21**, 189 (2021).
- [22] W. Pan, Y. Wang, Y. Wang, Z. Xia, F. S. Y. Yeung, M. Wong, H. S. Kwok, X. Wang, S. Zhang, L. Lu, *J. Alloys Compd.* **947**, 169509 (2023).
- [23] X.-L. Wang, Y. Shao, X. Wu, M.-N. Zhang, L. Li, W.-J. Liu, D.W. Zhang, S.-J. Ding, *RSC Adv.* **10**, 3572 (2020).
- [24] H. Xie, Y. Zhou, Y. Zhang, C. Dong, *Results Phys.* **11**, 1080 (2018).
- [25] Z. Zhu, W. Cao, X. Huang, Z. Shi, D. Zhou, W. Xu, *Micromachines* **13**, 617 (2022).
- [26] K. Park, J.H. Kim, T. Sung, H.-W. Park, J.-H. Baeck, J. Bae, K.-S. Park, S. Yoon, I. Kang, K.-B. Chung, H.-S. Kim, J.-Y. Kwon, *IEEE Trans Electron Devices* **66**, 457 (2019).
- [27] J. Raja, K. Jang, N. Balaji, J. Yi, *Semicond. Sci. Technol.* **28**, 115010 (2013).
- [28] J. Raja, K. Jang, N. Balaji, S. Qamar Hussain, S. Velumani, S. Chatterjee, T. Kim, J. Yi, *Mater. Sci. Semicond. Process* **37**, 129 (2015).
- [29] S.-P. Chang, D. Shan, *J. Nanosci. Nanotechnol.* **18**, 2493 (2018).
- [30] S. Cho, S. Kim, D. Kim, M. Yi, J. Byun, P. Song, *Coatings* **9**, 44 (2019).
- [31] H. C. Wu, T.-S. Liu, C.-H. Chien, *ECS Journal of Solid State Science and Technology* **3**, Q24 (2014).
- [32] D. Choi, B. Choi, *Proceedings of the International Display Workshops*, 527 (2019).
- [33] J. G. Um, J. Jang, *Appl. Phys. Lett.* **112**(16), 162104 (2018).
- [34] S. B. Eadi, H.-J. Shin, P. S. Kumar, K.-W. Song, R. Yuvakkumar, H.-D. Lee, *Chemosphere* **284**, 131287 (2021).
- [35] W. Zhang, P. Li, Y. Li, H. Chen, X. Wang, J. Ma, X. Zhao, *Thin Solid Films* **746**, 139121 (2022).
- [36] C. E. Benouis, M. Benhaliliba, A. Sanchez Juarez, M. S. Aida, F. Chami, F. Yakuphanoglu, *J. Alloys*

- Compd. **490**, 62 (2010).
- [37] M. Benhaliliba, C. E. Benouis, M. S. Aida, A. S. Juarez, F. Yakuphanoglu, A. T. Silver, J. Alloys Compd. **506**, 548 (2010).
- [38] K. Gueddouch, M. Zidane, R. Tamsamani, A. Mrigal, M. Addou, S. Ettami, Mater. Today Proc. **66**, 151 (2022).
- [39] M. Benhaliliba, Optik **241**, 167197 (2021).
- [40] J. S. Seo, J. H. Jeon, Y. H. Hwang, H. Park, M. Ryu, S. H. K. Park, B. S. Bae, Sci. Rep. **3**, 1 (2013).

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