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# Modifying subgap states with hydrogen incorporation from source/drain alloys for oxide phototransistors

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Keywords: Phototransistors Oxide semiconductor Hydrogen Thin-film transistors Subgap states	Phototransistors with amorphous oxide semiconductors (AOSs) have attracted considerable attention owing to their low leakage current density and process compatibility with the active array. In this study, we introduce hydrogen (H) from the source/drain electrodes to the active layer using a Ti-based alloy, specifically MoTi. The device with MoTi electrodes exhibits a more negatively shifted $V_{on}$ value of $-3.34$ V compared to the device with MoAl electrodes. The H in the oxide semiconductor passivates the oxygen vacancy states and generates additional deep states above the oxygen vacancy states. Consequently, phototransistors with MoTi electrodes
	domanterate a higher photoresponse under green and blue light

#### 1. Introduction

The demand for photosensors has increased because of their diverse applications such as healthcare systems and image-sensing devices that can replace the human eye. Photodiodes based on PN or Schottky junctions offer fast photoresponse times but have limitations such as relatively low photosensitivity and photoresponsivity [1]. Meanwhile, 3-terminal phototransistors can realize high performance because they can amplify the output signals through the control of gate voltages [2].

Amorphous oxide semiconductors (AOSs) have attracted considerable attention for application in phototransistors because of various advantages including low leakage current density, process compatibility with active matrices, and good uniformity [3]. However, typical AOSs have an optical band gap of over 3 eV, limiting their application to visible-light phototransistors requiring energy level from 1.6 to 3.1 eV [4,5]. Consequently, AOSs are commonly used in devices that detect ultraviolet (UV) light [6]. Several studies have reported the use of quantum dots (QDs) [7]. However, their fabrication has disadvantages such as degraded uniformity, complex fabrication processes, and vulnerability to the external environment. Therefore, the development of single-layer AOS-based phototransistors has become increasingly important.

Photoionization of intrinsic defects such as oxygen vacancies (V<sub>o</sub>), ionized oxygen interstitials [8], and incorporated hydrogen (H) [9] enables the generation of photoexcited charges in AOSs. Increasing the number of subgap states, more photoexcited carriers with low excitation energy can be generated, which is lower than the bandgap of the AOSs. In this study, we modified the subgap states by introducing H from the source/drain (S/D) region into the AOS, inducing the generation of H-related subgap states. Further, we utilized a titanium (Ti)-based alloy, specifically MoTi, as the S/D material because of its high affinity for H [10]. Consequently, S/D contains a relatively large amount of H, which induces the H diffusion into the AOS. To investigate the impact of H incorporation and subgap state formation on the properties of photo-transistors, we examined devices with an aluminum (Al)-based alloy, specifically MoAl, which can prevent H diffusion as previously investigated [11].

#### 2. Experiment

Back-channel-etched (BCE) structured phototransistors with different types of S/D electrodes were fabricated. First, an 80-nm-thick Mo was deposited using DC-sputter and patterned as the gate electrode. The gate insulator, consisting of a 200-nm-thick  $SiO_2$ , was deposited using PECVD at 300 °C. A 30-nm-thick Al:ITZO was used as the active layer because of its good chemical endurance, which is suitable for the BCE structure [12]. After that, an 80-nm-thick MoTi or MoAl was deposited using DC-sputter and patterned as the S/D electrode. The composition of deposited S/D alloys are  $Mo_{0.5}Ti_{0.5}$  and  $Mo_{0.7}Al_{0.3}$ , respectively. Finally, the devices were annealed at 230 °C under vacuum condition for 1 h. The schematic of the device is shown in Fig. 1a. For the measurements, three LED sources with central wavelengths of 455

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(blue), 530 (green), and 656 nm (red) were used.

#### 3. Results and discussion

Fig. 1b shows that the turn-on voltage ( $V_{on}$ ) of the phototransistor is influenced by the S/D material. The average  $V_{on}$  for the eight devices with MoAl and MoTi S/D are 0.17 and -3.34 V, respectively. Ti and its alloys can store more H because of their high affinities for H [13,14]. Consequently, the large amount of H in the MoTi S/D resulted in an increase in H. To compare the H content of the S/D materials, elastic recoil detection (ERD) at 2.0 MeV was conducted, and the results are shown in Fig. 1c and d. The extracted amount of H indicates that MoTi contains a larger amount of H than MoAl. Therefore, relatively more H can diffuse into the active when MoTi was used for S/D.

Fig. 2 shows the change in the transfer characteristics under blue, green, and red-light illumination at  $V_d$  of 10 V. Both devices exhibit  $V_{on}$  shifts under blue light. However, only the device with MoTi S/D exhibits green light detection, whereas the characteristics of the device with MoAl S/D barely changes. To evaluate the properties of the fabricated phototransistors, the photoresponsivity (PR) and photosensitivity (PS) were calculated using the following equations [15]:

$$PR = J_{photo}/P,$$
(1)

$$PR = I_{photo} / I_{dark}, \tag{2}$$

where  $J_{photo}$  is the photocurrent density and *P* is the power density of the incident light. The maximum PR and PS under green light were remarkably increased from 54.2 A/W and 33.6 to 427.5 A/W and 1.30 × 10<sup>6</sup>, respectively, when the S/D materials changed from MoAl to MoTi. Because the AOS has a relatively large optical bandgap, it cannot absorb red light, even with the highest power density in our equipment. However, owing to the presence of deep subgap states, photoexcitation can occur upon illumination with certain wavelengths of visible light. The phototransistors with MoTi S/D exhibited a higher photoresponse to green light, which originated from the additional subgap states within

the AOS.

The  $\Delta V_{\text{th}}$  under negative-bias illumination stress (NBIS) was measured to examine the subgap states in the AOS depending on the S/D materials. The  $\Delta V_{\text{th}}$  of the device with the MoTi electrode was smaller than that of the device with the MoAl electrode, as shown in Fig. 3a and b. Considering that NBIS degradation is mainly affected by Vo, the difference in  $\Delta V_{\text{th}}$  is attributed to the number of V<sub>o</sub> states in the AOS. It was previously reported that H in AOS can exist in various forms.  $H_i^+$  and  $H_0$ bonded to oxygen and Vo, respectively, are thermally stable and located above the conduction band minimum (CBM) [16]. The negatively shifted transfer characteristics of the phototransistor with the MoTi S/D indicate that H in the AOS donated electrons in the form of  $H_i^+$  and  $H_o^+$ . As the  $H_0^+$  states passivate  $V_0$ , the deep-energy state of the  $V_0$  is consequently decreased, as shown in Fig. 3c and d. Therefore, the device with MoTi S/D exhibited less  $\Delta V_{th}$  under NBIS because of the decrease in the hole trap center. However, the H in AOS can also exist as acceptor-like centers ( $H_i$  and H-DX<sup>-</sup>) by bonding with metal cations. The minimum energy required to excite electrons to the CBM was decreased because H- $DX^{-}$  is located above the  $V_0$  states [16]. Therefore, the phototransistor using MoTi S/D exhibited a higher PR than that using MoAl electrodes.

The time-dependent photoresponse was investigated by measuring  $I_d$  at  $V_G = -5.5$  V and  $V_D = 10$  V under the condition of 0.1-Hz periodic dark and blue/green light, as shown in Fig. 4.  $I_d$  increased dramatically when the blue/green light was illuminated and decreased rapidly in a short time, followed by a slow decay when the incident light was turned off. The slow decay can be attributed to persistent photoconductance (PPC) originating from the slow recombination of photoexcited electrons. PPC can typically be resolved by applying a short positive gate bias [15].

#### 4. Conclusions

In this study, we developed oxide phototransistors by modulating the subgap states via H incorporation from a Ti-based S/D. Phototransistors with MoTi S/D exhibited higher photoresponse and photosensitivity



Fig. 1. (a) Schematic of oxide phototransistors and (b) their transfer curves. H spectra obtained through ERD of (c) MoAl and (d) MoTi.



Fig. 2. Transfer curves of the device with MoAl S/D with illumination of (a) green, blue, and (b) red light. Transfer curves of the device with MoTi S/D with illumination of (c) green, blue, and (d) red light. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



**Fig. 3.** Δ*V*<sub>th</sub> under NBIS at different wavelengths of light illumination on the devices with (a) MoAl and (b) MoTi S/D. Schematic of the subgap states in AOS with (c) MoAl and (d) MoTi S/D.



Fig. 4. Time-dependent photoresponse of the phototransistor with MoTi S/D under 0.1-Hz periodic illumination of (a) blue and (b) green light. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

under green and blue light. The differences in the subgap states according to the S/D materials were inferred from the NBIS measurements. H in the AOS passivates  $V_0$ , resulting in well-behaved phototransistors with MoTi S/D, thereby exhibiting a higher photoresponse under lower visible light energy. The proposed phototransistors demonstrate improved photoresponse without the additional layers such as QDs. This characteristic is indicative of their have potential for integration into uniform active matrix image sensors.

#### CRediT authorship contribution statement

Wooseok Jeong: Conceptualization, Methodology, Visualization, Writing – original draft. Seong-In Cho: Formal analysis, Investigation. Sang-Hee Ko Park: Writing – review & editing, Funding acquisition. Jong Beom Ko: Conceptualization, Writing – review & editing, Visualization, Supervision.

#### **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Data availability

Data will be made available on request.

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#### References

[1] N. Liu, H. Tian, G. Schwartz, J.B.H. Tok, T.L. Ren, Z.N. Bao, Large-area, transparent, and flexible infrared photodetector fabricated using p-n junctions formed by n-doping chemical vapor deposition grown graphene, Nano Lett. 14 (7) (2014) 3702–3708, https://doi.org/10.1021/nl500443j.

- [2] Y.B. Guo, L. Zhu, W.T. Gao, Z.Y. Ren, H. Xiao, Z.Y. Ge, Low-voltage protonic/ photonic synergic coupled oxide phototransistor, Org. Electron. 71 (2019) 31–35, https://doi.org/10.1016/j.orgel.2019.04.038.
- [3] H. Yoo, Y.J. Tak, W.G. Kim, Y.G. Kim, H.J. Kim, A selectively processible instant glue passivation layer for indium gallium zinc oxide thin-film transistors fabricated at low temperature, J. Mater. Chem. C 6 (38) (2018) 10376, https://doi.org/ 10.1039/c8tc90192a.
- [4] D.C. Hays, B.P. Gila, S.J. Pearton, F. Ren, Energy band offsets of dielectrics on InGaZnO4, Appl. Phys. Rev. 4 (2017) 2, https://doi.org/10.1063/1.4980153.
- [5] Y.S. Shiah, et al., Mobility-stability trade-off in oxide thin-film transistors, Nat. Electron. 4 (11) (2021) 800–807, https://doi.org/10.1038/s41928-021-00671-0.
   [6] S. Knobelsnies, et al. Elexible a-IGZO phototransistor for instantaneous and
- [6] S. Knobelspies, et al., Flexible a-IGZO phototransistor for instantaneous and cumulative UV-exposure monitoring for skin health, Adv. Electron. Mater. 2 (2016) 10, https://doi.org/10.1002/aelm.201600273.
- [7] S.W. Shin, K.H. Lee, J.S. Park, S.J. Kang, Highly transparent, visible-light photodetector based on oxide semiconductors and quantum dots, ACS Appl. Mater. Inter. 7 (35) (2015) 19666–19671, https://doi.org/10.1021/acsami.5b04683.
- [8] S. Lee, A. Nathan, S. Jeon, J. Robertson, Oxygen defect-induced metastability in oxide semiconductors probed by gate pulse spectroscopy, Sci. Rep. 5 (2015) 14902, https://doi.org/10.1038/srep14902.
- [9] J. Kim, et al., Al<sub>2</sub>O<sub>3</sub>-induced sub-gap doping on the igzo channel for the detection of infrared light, ACS Appl. Electron. Mater. 2 (2020) 1478–1483, https://doi.org/ 10.1021/acsaelm.0c00228.
- [10] Q.Q. Wang, et al., Mechanism of hydrogen-induced defects and cracking in Ti and Ti-Mo alloy, Int. J. Hydrogen Energ. 48 (2023) 5801–5809, https://doi.org/ 10.1016/j.ijhydene.2022.11.119.
- [11] W. Jeong, et al., Suppressing channel-shortening effect of self-aligned coplanar Aldoped In-Sn-Zn-O TFTs using Mo-Al alloy source/drain electrode as Cu diffusion barrier, J. Alloy. Compd. 859 (2021), 158227, https://doi.org/10.1016/j. jallcom.2020.158227.
- [12] S.H. Cho, et al., Highly stable, high mobility Al:SnZnInO back-channel etch thinfilm transistor fabricated using PAN-based wet etchant for source and drain patterning, IEEE Trans. Electron. Dev. 62 (2015) 3653–3657, https://doi.org/ 10.1109/Ted.2015.2479592.
- [13] A. Lopez-Suarez, J. Rickards, R. Trejo-Luna, Analysis of hydrogen absorption by Ti and Ti-6Al-4V using the ERDA technique, Int. J. Hydrogen Energ. 28 (2003) 1107–1113, https://doi.org/10.1016/S0360-3199(02)00202-1.
- [14] S. Ghosh, V. Padmanabhan, Hydrogen storage in titanium-doped single-walled carbon nanotubes with Stone-Wales defects, Diam. Relat. Mater. 77 (2017) 46–52, https://doi.org/10.1016/j.diamond.2017.05.013.
- [15] H. Yoo, et al., A review of phototransistors using metal oxide semiconductors: research progress and future directions, Adv. Mater. 33 (2021) 47, https://doi.org/ 10.1002/adma.202006091.
- [16] Y. Kang, et al., Hydrogen bistability as the origin of photo-bias-thermal instabilities in amorphous oxide semiconductors, Adv. Electron. Mater. 1 (2015) 7, https://doi. org/10.1002/aelm.201400006.