The effect of charge transfer transition on the photostability of lanthanide-doped indium oxide thin-film transistors

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Amorphous oxide semiconductors are promising for their use in thin-film transistor (TFT) devices due to their high carrier mobility and large-area uniformity. However, their commercialization is limited by the negative gate bias stress experienced under continuous light illumination. Here, we report an approach to improve the negative bias illumination stress (NBIS) stability of amorphous oxide semiconductors TFTs by using lanthanide-doped indium oxide semiconductors as the channel layer. The effect of different lanthanide dopants on performances of solution-processed Ln:In₂O₃ TFTs are investigated. All lanthanides exhibit strong suppression of oxygen vacancy, which shift the \( V_{on} \) from \(-13.5\) V of pure In₂O₃ TFT to \(-1\) to \(-1.1\) V of Ln:In₂O₃ TFTs (except Ce). However, only Pr:In₂O₃ and Tb:In₂O₃ TFTs exhibit much better NBIS stability with same \( \Delta V_{on} \) of \(-3.0\) V, compared to much higher \( \Delta V_{on} \) of \(-7.9\) to \(-15.6\) V for other Ln:In₂O₃ TFTs. Our comprehensive study reveals that praseodymium and terbium act as a blue light down-conversion medium with low charge transfer transition energy for lowering photosensitivity of oxide semiconductors.

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Amorphous oxide semiconductors (AOSs) have attracted considerable attention, owing to their outstanding properties, such as high carrier mobility with large-area uniformity, low off-state current (I_{on/off}), and large optical bandgap. However, there is a serious issue limiting further commercialization applications of AOS TFTs that serious threshold voltage shift ($\Delta V_{th}$) is observed when the TFTs experience a negative gate bias stress combined with continuous light illumination even in the visible spectrum (NBIS), which cannot be fully recovered even after removing the stress for days. It is widely accepted that the NBIS instability is attributed to the intrinsic states of AOS materials regardless of the device structures. Several degradation models are proposed to reveal the mechanism of the NBIS instability of the AOS TFTs, including the trapping of photogenerated holes, the formation of ionized oxygen vacancy (Vo) defects, the self-trapping of holes by polarons, etc.

To improve the NBIS stability of AOS TFTs, reducing concentration of preexisting Vo defects (subgap states) is the most commonly used method. J. Kim and H. Hosono et al. developed a wide-bandgap AOS (ZnGaO) to improve the NBIS stability of the AOS TFTs by widening the optical bandgap and the potential supply of oxygen species, such as high-pressure annealing (HPA), oxygen-containing plasma treatment, ozone radical treatment, and ultra-high vacuum sputtering, would result in a decrease in Vo. However, the improved Vo shift is still too large to drive active-matrix displays without compensation. J. Kim and H. Hosono et al. developed a wide-bandgap AOS (ZnGaO) to improve the NBIS stability of the AOS TFTs by widening the optical bandgap and the conduction band minimum (CBM) larger than ~3 eV. However, this approach will decrease the mobility seriously, because the 4$s$ orbitals of adjacent metal ions (both Ga and Zn) do not overlap that would destroy the electron transport paths in the amorphous state. Therefore, there is a tradeoff between the mobility and NBIS stability of the AOS TFTs.

Here, we report an approach to improve the NBIS stability of AOS TFTs by using lanthanide-doped indium oxide (Ln:In$_2$O$_3$) semiconductors as the channel layer. It is found that only praseodymium (Pr) and terbium (Tb) can improve the NBIS stability of the AOS TFTs greatly, and doping Pr/Tb into In$_2$O$_3$ would not affect the mobility much, so the tradeoff between the mobility and NBIS stability of the AOS TFTs can be broken. Comprehensive studies reveal that different lanthanides (Ln) have a different effect on the NBIS stability of AOS TFTs, and Pr/Tb acts not only a Vo suppressant but also a blue light downconversion medium.

**Results and discussion**

The absorption characteristics of the different Ln ions. As known, lanthanides have electron configurations of [Xe] 4f$^n$5d$^m$6s$^2$ ($n = 0–14$, $m = 0–10$). The unfilled 4$f$ orbitals form complicated energy level structures due to Coulomb interactions, spin-orbit coupling, and external field interactions. Lanthanides exhibit various optical properties which are attributed to $f-f$ transition, $f-d$ transition, or charge transfer transition (electrons transit between the ligands and Ln ions). Figure 1 shows the photos of the different aqueous Ln(NO$_3$)$_3$·nH$_2$O solutions (0.4 M) and the corresponding spin-coated thin films annealed at 300 °C. Only Pr(NO$_3$)$_3$·nH$_2$O, Nd(NO$_3$)$_3$·nH$_2$O, Ho(NO$_3$)$_3$·nH$_2$O, and Er(NO$_3$)$_3$·nH$_2$O solutions show light colors, which are attributed to the $f-f$ transition of the Pr, Nd, Ho, and Er ions. Figure 2a shows the absorption spectra of the different aqueous Ln(NO$_3$)$_3$·nH$_2$O solutions. Typical $f-f$ sharp absorption peaks are seen in Pr(NO$_3$)$_3$·nH$_2$O, Nd(NO$_3$)$_3$·nH$_2$O, Ho(NO$_3$)$_3$·nH$_2$O, and Er(NO$_3$)$_3$·nH$_2$O solution (much weaker absorption peaks are also seen in Sm(NO$_3$)$_3$·nH$_2$O, Eu(NO$_3$)$_3$·nH$_2$O, Dy(NO$_3$)$_3$·nH$_2$O, and Tm(NO$_3$)$_3$·nH$_2$O solutions), which are in consistent with the colors of the solutions.

Interestingly, after the precursors are spin-coated onto the glass substrates and annealed at 300 °C, all the films are colorless and transparent except PrO$_x$ and TbO$_x$. To investigate the color difference between the solution and the corresponding film, UV-visible light absorption was measured for all of the LnO$_x$ films, as shown in Fig. 2b. The CeO$_x$, PrO$_x$, and TbO$_x$ films exhibit broadband absorption, while the other films are transparent to the light with the wavelength longer than 300 nm. For the CeO$_x$ film, the absorption is strong with a peak centered at ~300 nm and a cut-off edge at ~390 nm. For the PrO$_x$ and TbO$_x$ films, the absorption peaks are broadened into the visible light without distinct cut-off edges. The broadband and strong absorption implies that the absorption cannot be caused by $f-f$ transition, because $f-f$ transition has some features, including i) $f-f$ transition is forbidden due to the same parity, so the $f-f$ transition absorption is relatively weak; ii) $f-f$ transition spectrum is line spectrum with sharp peaks because the intimal 4$f$ orbitals are screened by the outer 5$d$ and 6$s$ orbitals and hardly influenced by the chemical environment; iii) $f-f$ transition can be observed in most of the Ln ions. The absorption spectra of CeO$_x$, PrO$_x$, and TbO$_x$ films is similar to that reported by D.E. Hobart et al. in 1980 (see Fig. 2c–e), which ascribed the broadband and absorption to the charge transfer transition between the delocalized ligand molecular orbital and the Ln$^{4+}$ ion. Therefore, it is reasonable to deduce that Ce$^{4+}$, Pr$^{4+}$, and Tb$^{4+}$ ions exist in the solid films but cannot exist in the aqueous Ln(NO$_3$)$_3$·nH$_2$O solutions. The oxidation from Ln$^{3+}$ to Ln$^{4+}$ is considered to be taken place during the 300 °C annealing step because all of the as-spin-coated LnO$_x$ films without annealing are colorless and transparent. As known, nitrate (NO$_3^-$) can releases oxygen-free radicals at a relatively low temperature (~200 °C). The oxygen radicals with strong oxidability can help oxidizing the Ce$^{3+}$, Pr$^{3+}$, and Tb$^{3+}$ ions to the tetravalent oxidation state. Compared to the work by D.E. Hobart et al., the absorption spectra for the PrO$_x$ and TbO$_x$ films in this work span a much wider range (extend to the near-infrared region), which may be attributed to the larger metal-ligand electron cloud overlap in the solid state. Moreover, the oxygen vacancies and structural defects of the amorphous LnO$_x$ films will give rise to the electron cloud expansion effect and further broaden the absorption spectra to the near-infrared region, as discussed later.

To further analyze, the valence state of the CeO$_x$, PrO$_x$, and TbO$_x$ films, X-ray photoelectron spectroscopy (XPS) experiments were carried out, as shown in Supplementary Fig. 1. It can be found that the Ce ions in the CeO$_x$ film are mainly in the tetravalent state (Ce$^{4+}$) with only a small part of trivalent Ce ions (Ce$^{3+}$, see V$\prime$-V$\prime$$^\prime$ peaks in Supplementary Fig. 1), while the number of Pr$^{3+}$/Tb$^{3+}$ ions is comparable to that of Pr$^{4+}$/Tb$^{4+}$ ions in the PrO$_x$/TbO$_x$ films (Supplementary Fig. 1).
**Fig. 1 Ln(NO)_3·nH_2O aqueous solutions and LnO_x films.** The photos of the different aqueous Ln(NO)_3·nH_2O solutions (0.4 M) and the corresponding spin-coated films annealed at 300 °C.

**Fig. 2 The absorption of Ln(NO)_3·nH_2O aqueous solutions and LnO_x films.** a the absorption spectra of the different Ln(NO)_3·nH_2O and In(NO)_3·nH_2O aqueous solutions. b UV-visible light absorption of the different LnO_x films based on spin-coating Ln(NO)_3·nH_2O aqueous solutions annealed at 300 °C. c-d UV-visible light absorption of c Ce^{3+} and CeO_x, d Pr^{3+} and PrO_x, and e Tb^{3+} and TbO_x.
form precursor solutions. The In/Ln molar ratio was optimized to be 19:1 (5 at.% of Ln). Bottom-gate and top-contact TFTs with undoped \( \text{In}_2\text{O}_3 \) or Ln:In\(_2\text{O}_3 \) channel layers were fabricated by spin-coating In\(_2\text{O}_3 \) or Ln:In\(_2\text{O}_3 \) aqueous precursor solutions and annealing at 300/350 °C in air condition for 1 h (see Fig. 3a). To avoid the influence of the air molecules on the stability of the AOS TFTs, all the TFTs were tested under vacuum condition.

Figure 3c, d show output and transfer characteristics of the undoped In\(_2\text{O}_3 \) TFT. The mobility is extracted from transfer characteristics at \( V_{GS} = 1.1 \) and 15.1 V, respectively, and \( V_{GS} \) swept from −30 to 30 V, while output characteristics were tested when \( V_{GS} \) was held at different voltages between 0 and 30 V in step of 5 V, and \( V_{DS} \) swept from 0 to 30 V at each \( V_{GS} \).

The transfer characteristic of the AOS TFTs based on Ln:In\(_2\text{O}_3 \). Figure 4 shows the transfer characteristic curves of the TFTs based on 14 Ln:In\(_2\text{O}_3 \) annealed at 300 °C. All the TFTs exhibit excellent gate-controlled field-effect characteristics except Ce:In\(_2\text{O}_3 \) TFT (see Supplementary Fig. 2) that will be discussed later. Compared to the undoped In\(_2\text{O}_3 \) TFT, which has a \( V_{on} \) of −13.3 V, the Ln:In\(_2\text{O}_3 \) TFTs have more positive \( V_{on} \) that range from −1 to 1 V (see Table 1) and steeper SS, revealing that Ln doping with a concentration of only 5 at.% can suppress Vo generation and decrease free carrier concentration substantially.

**Table 1 Summary for the performance of TFTs with Ln:In\(_2\text{O}_3 \)** channels.

| Dopant | \( \mu \) at 350 °C (cm\(^2\) V\(^{-1}\) S\(^{-1}\)) | \( V_{on} \) (V) | \( \mu \) at 300 °C (cm\(^2\) V\(^{-1}\) S\(^{-1}\)) | \( V_{on} \) (V) | NBIS \( \Delta V_{on} \) (V) |
|--------|---------------------------------|-----------------|---------------------------------|-----------------|----------------|
| La     | 8.3                             | −4.1            | 3.5                             | −1.0            | −7.9           |
| Ce     | −                               | −                | −                               | −               | −              |
| Pr     | 12.2                            | −3.7            | 4.3                             | −0.5            | −3.0           |
| Nd     | 8.2                             | −1.7            | 3.1                             | 1.0             | −8.0           |
| Sm     | 13.7                            | −5.6            | 4.2                             | 0.1             | −12.4          |
| Eu     | 7.6                             | −3.2            | 4.3                             | −0.4            | −12.8          |
| Gd     | 16.2                            | −6.9            | 4.7                             | −0.2            | −13.9          |
| Tb     | 12.7                            | −3.2            | 5.2                             | −0.8            | −3.0           |
| Dy     | 15.3                            | −3.4            | 4.3                             | −0.2            | −15.6          |
| Ho     | 14.8                            | −3.7            | 4.0                             | −0.4            | −11.9          |
| Er     | 13.2                            | −3.6            | 4.7                             | −1.0            | −9.0           |
| Tm     | 10.1                            | −3.5            | 6.1                             | −0.1            | −14.7          |
| Yb     | 6.0                             | −3.9            | 4.8                             | −0.8            | −14.9          |
| Lu     | 14.3                            | −3.5            | 4.1                             | −0.5            | −11.9          |
In conventional AOS (IGZO), the concentration of the free carrier suppressant (Ga) should be very high (33.3 at.%), because Ga is not a strong free carrier suppressant. The electronegativity of Ga is 1.6 with Ga–O dissociation energy of 374 kJ mol$^{-1}$, no much difference compared to In (the electronegativity of In is 1.7 with In–O dissociation energy of 346 kJ mol$^{-1}$). High Ga concentration will destroy overlaying of the In 5$s$ orbitals (especially in the amorphous state), and result in electron mobility decrease. Instead, the lanthanides are a strong carrier suppressant, because their electronegativity (1.10–1.27, Supplementary Table 1) is much lower than Ga, and the In–O dissociation energy (397–799 kJ mol$^{-1}$, Supplementary Table 1) is much higher than Ga–O. To characterize the effect of Ln doping on the Vo concentration, XPS measurements of O 1$s$ of undoped In$_2$O$_3$ and 14 Ln:In$_2$O$_3$ films were performed, as shown in Supplementary Fig. 3. The O 1$s$ spectra can be fitted by three Gaussian distributions with binding energies at 529.5 ± 0.2 eV (Peak 1), 530.0 ± 0.2 eV (Peak 2), and 531.3 ± 0.3 eV (Peak 3), corresponding to the oxygen in oxide lattices (M–O–M), oxygen vacancies (Vo) and metal hydroxide (or loosely bound oxygen) species (M–OH), respectively$^{36}$. The Vo/(M–O–M + Vo + M–OH) ratio for undoped In$_2$O$_3$ film is 18.3 %, while those for Ln:In$_2$O$_3$ (except Ce:In$_2$O$_3$) films are in the range of 10.8–4.1 %. The results prove that the Ln doping can effectively suppress Vo generation. It is worth noting that high-intensity M–OH peaks are observed in the XPS spectra of the La:In$_2$O$_3$ and Pr:In$_2$O$_3$ films, which may be attributed to larger radii of La$^{3+}$ and Pr$^{3+}$ compared to other trivalent Ln ions (except Ce which is mainly in the tetravalent state). Larger radius difference between In$^{3+}$ and Ln$^{3+}$ would cause more serious lattice mismatch and more loosely bound oxygen species. Interestingly, the Ce:In$_2$O$_3$ film has an extremely low Vo ratio of only 7.8% that is ascribed to the strong reducibility of Ce$^{3+}$, which will further bind with oxygen atoms and oxidized to Ce$^{4+}$ during annealing. Because the Vo concentration is very low in the Ce:In$_2$O$_3$ film, the free carrier density of it is very low, so almost no field effects are found in the Ce:In$_2$O$_3$ TFTs. It should be noted that decreasing the Ce doping concentration will increase the $I_{on}$ but will make the $V_{on}$ more negative, as shown in Fig. S2. It is clear that doping Ce into In$_2$O$_3$ (in solution method) will deteriorate the performances of the Ce:In$_2$O$_3$ TFT (even with a small Ce doping amount of 0.8 at.%).

The mobilities of the TFTs based on 13 Ln:In$_2$O$_3$ (except Ce:In$_2$O$_3$) semiconductors are 3.1–6.1 cm$^2$ V$^{-1}$ s$^{-1}$ when annealed at 300 °C and 8.2–16.2 cm$^2$ V$^{-1}$ s$^{-1}$ when annealed at 350 °C (see Table 1 and Supplementary Fig. 4). The higher mobility with higher annealing temperature is attributed fewer impurities and a higher degree of order. Further increase the annealing temperature (>350 °C) has not tried, because the electrodes will be oxidized at higher annealing temperature. It can be seen from Table 1 that the mobility of the Eu:In$_2$O$_3$ and Yb:In$_2$O$_3$ TFTs are particularly low that may be due to the special electronic configurations of Eu (4$f^7$6$s^2$) and Yb (4$f^{14}$6$s^2$), which may lose two 6$s$ electrons and form relatively stable Eu$^{2+}$ (4$f^7$) and Yb$^{2+}$ (4$f^{14}$). However, there are no direct evidences that Eu$^{2+}$ and Yb$^{2+}$ ions exist in the annealed solid films.

It is worth noting that the mobility of solution-processed AOS TFTs is generally lower than that of vacuum-based AOS TFTs because of the lower film quality and the impurities induced by the precursors. In our previous studies, the mobility of the vacuum-based Nd:In$_2$O$_3$ (5 at.%) TFT can reach as high as 46.4 cm$^2$ V$^{-1}$ s$^{-1}$, while the mobility of the solution-processed Nd:In$_2$O$_3$ (2 at.%) TFT is only 15.6 cm$^2$ V$^{-1}$ s$^{-1}$ as shown in Supplementary Fig. 5. Both films exhibit clear nanocrystalline nature with In$_2$O$_3$ bixbyte structure, which is consistent with the standard value for bulk cubic-In$_2$O$_3$. Therefore, 5 at.% of Ln doping will not have a remarkable effect on the mobility of the In$_2$O$_3$. 

Fig. 4 Transfer characteristics of Ln:In$_2$O$_3$ TFTs. Transfer characteristics of TFTs based on spin-coating Ln:In$_2$O$_3$ aqueous precursor solutions with annealing at 300 °C in air condition, the $V_{DS}$ was held at 1.1 V (red curve) and 15.1 V (black curve), respectively, and the $V_{GS}$ sweep from –30 to 30 V.
The NBIS stability of the Ln:In$_2$O$_3$ TFTs. Supplementary Figure 6 shows the evolutions of transfer curves of the TFTs illuminated with different intensity of white light (without bias stress). The schematic diagram and the photo of the photo-stability testing equipment are shown in Supplementary Fig. 6. During illumination, the TFT channel was directly exposed to white LED light whose spectrum is depicted in Fig. 3b, and the intensity of the white light ranges from 500 to 5000 Lux. The undoped In$_2$O$_3$ TFT is rather unstable under the white light illumination, while the Pr:In$_2$O$_3$ and Tb:In$_2$O$_3$ TFTs are hardly affected by the white light illumination (highly stable even under 5000-Lux-light illumination, see Supplementary Fig. 7). For further investigating the effect of Ln doping on the photostability of the AOS TFTs, the devices were tested under the NBIS. During the NBIS, the TFTs were bias with a $V_{GS}$ of $-20$ V under continuous white LED irradiation (250 Lux), and the transfer curves were recorded at 0, 100, 600, 1200, and 3600 s, respectively. Figure 5 shows the evolutions of the transfer curves of different TFTs as a function of the stress time. The $V_{on}$ shift ($\Delta V_{on}$) of the undoped In$_2$O$_3$ TFT is as large as $-12.5$ V (not shown), and the $\Delta V_{on}$ of the 13 Ln:In$_2$O$_3$ (except Ce:In$_2$O$_3$) TFTs are summarized in Table 1 and Supplementary Fig. 8. It is observed that the NBIS of the Pr:In$_2$O$_3$ and Tb:In$_2$O$_3$ TFTs are improved greatly, with the same $\Delta V_{on}$ of $-3.0$ V. The $\Delta V_{on}$ of the other 11 Ln:In$_2$O$_3$ TFTs are at the range of $-7.9$ to $-15.6$ V (see Table 1). The result shows that only the Pr and Tb are effective dopants for resolving the NBIS instability problem of the AOS TFTs.

It is known that high-density subgap states are formed by Vo existed in AOSs near valance band maximum (VBM). Under light illumination, some of the Vo will be thermal excited and lose two electrons and become Vo$^{2+}$. The transition of the Vo ground state to Vo$^{2+}$ excited states causes spontaneous outward relaxation, which makes the Vo$^{2+}$ level act as a subgap state below the conduction band minimum (CBM), contributing the delocalized free electrons in the conduction band,$^{38-40}$ as illustrated in Fig. 6. It has been reported that the formation energy of Vo$^{2+}$ decreases as the fermi lever ($E_F$) approaching the VBM$^{38}$. When a negative bias is applied to the gate electrode, the energy band at the gate insulator (GI)/AOS interface bends up, so the $E_F$ is closer to the VBM (see Fig. 6). As a result, the formation energy of Vo$^{2+}$ at the GI/AOS interface decreases. Therefore, more Vo$^{2+}$ will be formed when a negative $V_{GS}$ is applied during light illumination (NBIS), leading to more electrons in the conduction band, which is the reason for the large negative $V_{on}$ shift under the NBIS. Meanwhile, the $\Delta V_{on}$ is increase with illumination intensity (as seen in Supplementary Fig. 9). The photoresponse is reversible very slowly with a time constant exceeding thousands of seconds. This is attributed to the
relaxation of metastable donor states with activation energies of 0.9–1.1 eV.\(^3,4\)

The effect of Pr and Tb in NBIS stability. It can be deduced from the analysis above that there are mainly three ways to improve the NBIS stability of the AOS TFTs. i) to decrease the \(V_o\) concentration; ii) to widen the bandgap of the AOSs and deepen the VBM and the \(V_o\) subgap states, so that the \(V_o\) cannot be activated by the visible light; iii) to downconvert the incident light by doping some lanthanide ions into the AOSs, so that the energy of the output light is not enough to activate the \(V_o\). Here, the excellent NBIS stability of the Pr:In\(_2\)O\(_3\) and Tb:In\(_2\)O\(_3\) TFTs cannot be attributed to the suppression of \(V_o\), because there is no evident relationship between the \(V_o\) ratios and the \(\Delta V_{on}\) under the NBIS (see Table 1 and Supplementary Table 1). The VBMs of the Ln:In\(_2\)O\(_3\) films were characterized by ultraviolet photoelectron spectroscopy (UPS) measurements. It is found that there is no much difference on the VBMs for all of the 14 Ln:In\(_2\)O\(_3\) films (Supplementary Fig. 10), so the much better NBIS stability of the Pr:In\(_2\)O\(_3\) and Tb:In\(_2\)O\(_3\) TFTs compared to the other Ln:In\(_2\)O\(_3\) TFTs cannot be attributed to the bandgap widening. Therefore, the excellent NBIS stability of the Pr:In\(_2\)O\(_3\) and Tb:In\(_2\)O\(_3\) TFTs is probably due to the downconversion effect of the Pr and Tb ions.

As discussed at the beginning of this section, the CeO\(_x\), PrO\(_x\), and TbO\(_x\) films exhibit broad-band absorption (see Fig. 2), while the other films are transparent to the light with the wavelength longer than 300 nm; and the broad-band and strong absorption the CeO\(_x\), PrO\(_x\), and TbO\(_x\) films are mainly resulted from the charge transfer transition from ligands to Ln \(4f\). Among all of the lanthanides, only Ce, Pr, Tb, Nd, and Dy have tetravalent oxidation states, but Nd\(^{4+}\) and Dy\(^{4+}\) are very unstable because of their large III–IV potentials (\(E_0^0\), see Supplementary Table 1).\(^41\) The stability sequence of the tetravalent oxidation states is Ce\(^{4+}\) > Tb\(^{4+}\) = Pr\(^{4+}\) ≈ Nd\(^{4+}\) > Dy\(^{4+}\). In lanthanide oxides, the Ln5\(_d\) orbitals and the O2\(_p\) orbitals make up the chemical bonds; the bonding orbitals form the valance band (VB), and antibonding orbitals form the conduction band (CB), as illustrated in Fig. 7. So, the charge transfer energy (\(E_{CT}\)) is the difference between the ground state of the Ln\(^{3+}\) (\(E_{ground}\)) and the energy level of VBM (\(E_V\)):

\[
E_{CT} = E_{ground}(\text{Ln}^{3+}) - E_V \tag{1}
\]

The \(E_{CT}\) of Ce (III–IV) can be calculated from the charge transfer absorption peak (300 nm, see Fig. 2c) to be 4.1 eV. The \(E_{CT}\) of Pr (III–IV) and Tb (III–IV) should be estimated from the \(E_{CT}\) of Ce (III–IV), because the PrO\(_x\) and TbO\(_x\) do not display a
well-resolved charge transfer absorption band (Figs. 2d, e). L.J. Nugent et al.\textsuperscript{44} reported that there is a linear unit-slope relationship between the III–IV potentials (\(E^0\)) and the first charge transfer band energy. Although they did not provide the formulas for the relationship between the \(E_{\text{CT}}\) and \(E^0\), it can be deduced from plots of the \(E^0\) versus the first absorption energy that \(E_{\text{CT}}\) of Pr/Tb can be expressed as

\[
E_{\text{CT}}(\text{Ln}) = E_{\text{CT}}(\text{Ce}) + C[E^0(\text{Ce}) - E^0(\text{Ln})] \tag{2}
\]

where \(C\) is a constant estimated to be \(-1\, \text{eV}^{-1}\). It can be calculated from Eq. 2 that \(E_{\text{CT}}\) of Pr and Tb (III–IV) are 2.5 eV (496 nm) and 2.6 eV (477 nm), respectively. Therefore, the charge transfer absorption peaks of PrO\(_x\) and TbO\(_x\) enter the blue light peak centered at \(~625\, \text{nm}\). So it can be deduced that the light-induced shallow electron traps in O\(_2\)++ films should be greater than 3.18 eV (<390 nm). It means that the visible light absorption of the CeO\(_x\) can be lower greatly by choosing ligands with lower electronegativity due to the larger metal-ligand electron cloud overlap (electron cloud expansion effect). Different from the \(f\, f\) transition, the \(f\, d\) transition is allowed by the parity selection rule, so it has a fairly high transition intensity that is 10\(^6\) times higher than \(f\, f\) transition. And \(f\, d\) transition has a wide absorption band because the 5d energy level is widened by ligand ions. Since the \(E_{\text{f}}\) for Ce\(^{3+}\) is lower than that for Pr\(^{3+}\) or Tb\(^{3+}\), and the light absorption spectrum of the CeO\(_x\) film is cut-off at \(~390\, \text{nm}\) (Fig. 1e), it can be deduced that the light energy for the \(f\, d\) transition for all of the CeO\(_x\), PrO\(_x\), and TbO\(_x\) films should be greater than 3.18 eV (<390 nm). It means that the visible light absorption of the PrO\(_x\) and TbO\(_x\) films cannot be attributed to the \(f\, d\) transition. Therefore, the charge transfer transition is the only reason for the greatly improved NBIS stability of the TFTs with the Pr:In\(_2\)O\(_3\) or Tb:In\(_2\)O\(_3\) semiconductor layers.

It is worth noting that the bivalent Ln ions (Ln\(^{2+}\)) have lower \(E_{\text{f}}\) than the trivalent Ln ions (Ln\(^{3+}\)). And the \(E_{\text{f}}\) of some Ln\(^{2+}\) ions are close to the energy of blue light. For example, the \(E_{\text{f}}\) for Eu\(^{2+}\), Yb\(^{2+}\), Sm\(^{2+}\), and Tm\(^{2+}\) are 4.30, 4.20, 2.92, and 2.87 eV, respectively (see Fig. 9b). However, only Eu\(^{2+}\) and Yb\(^{2+}\) are stable in the solid state. Moreover, the Ln\(^{2+}\) ions must experience high-temperature annealing (>300 °C), so the Ln\(^{2+}\) ions will be oxidized to Ln\(^{3+}\) ions. Thus, it is difficult to achieve stable AOS TFTs doped with Ln\(^{2+}\) ions.

It is worth noting that the Pr:In\(_2\)O\(_3\) and Tb:In\(_2\)O\(_3\) TFTs exhibit worsened stability under positive bias illumination stress (PBIS) with \(\Delta V_{\text{on}}\) of 1.1 and 0.9 V, respectively (see Supplementary Fig. 12). The degradation of the PBIS for Pr:In\(_2\)O\(_3\) and Tb:In\(_2\)O\(_3\) TFTs is ascribed to the light-induced shallow electron traps (possibly Pr\(^{3+}\) and Tb\(^{3+}\) related defects).
Supplementary Figures 13 and 14 show the stability under negative bias temperature stress (NBTS) and positive bias temperature stress (PBTS) of different TFTs at 60 °C without light illumination, respectively. The ΔV_{on} for all the TFTs under NBTS, PBTS, and PBIS are summarized in Supplementary Table 2. The pure In_{2}O_{3} TFT exhibits poor NBTS stability, while all of the Ln:In_{2}O_{3} TFTs have good NBTS stability. In contrast to the NBTS stability, the PBTS stability of the pure In_{2}O_{3} TFT is good (see Supplementary Fig. 14), which may be attributed to the much higher free electron density than the electron traps in the In_{2}O_{3} film. However, most Ln:In_{2}O_{3} TFTs show relatively poor PBTS (especially the La, Nd, and Ho incorporated In_{2}O_{3} TFTs). It reveals that incorporating Ln to In_{2}O_{3} will induce shallow electron traps in the In_{2}O_{3} films. The temperature effect of the Ln:In_{2}O_{3} TFTs is still under investigated, and will be published in the future.

Conclusions
In conclusion, the effect of different lanthanide dopants on the NBIS stability of solution-processed AOS TFTs are investigated. Compared to the undoped In_{2}O_{3} TFT, which has a turn-on voltage (V_{on}) of −13.3 V, the lanthanide-doped In_{2}O_{3} (Ln:In_{2}O_{3}) TFTs have more positive V_{on} that range from −1 to 1 V and more steeper SS, revealing that Ln doping with a concentration of only 5 at.% can suppress oxygen vacancy (Vo) generation and decrease free carrier concentration substantially. More interestingly, the NBIS stability of the TFTs are improved greatly when the In_{2}O_{3} AOS is doped by praseodymium (Pr) or terbium (Tb). The Pr:In_{2}O_{3} and Tb:In_{2}O_{3} TFTs exhibit the same V_{on} shift (ΔV_{on}) of −3.0 V, compared to a ΔV_{on} of as high as −12.0 V of the undoped In_{2}O_{3} TFT. The NBIS stability of the In_{2}O_{3} TFTs doped with lanthanides is not good, with a ΔV_{on} of at the range of −7.9 to −15.6 V. The mobility and the stability of solution-processed Pr:In_{2}O_{3} and Tb:In_{2}O_{3} TFTs are 12.2 and 12.7 cm² V⁻¹ s⁻¹, respectively. Comprehensive studies reveal that Pr/Tb acts as not only a Vo suppressant but also a blue light downconversion medium with low charge transfer transition energy. Most of the incident white light can be absorbed by Pr⁴⁺ or Tb³⁺ ions by charge transfer transition, and downconverted to nonradiative transition or red light. As a result, the NBIS stability of the AOS TFTs is improved greatly. The result is different from those reported elsewhere, where the lanthanides are merely regarded as free carrier suppressants of the AOSs due to ultra-low electronaffivities.

Methods
Materials. The oxide semiconductor films were deposited by spin-coating and thermal decomposition of precursors solution. A 0.2 M In_{2}O_{3} solution was prepared by dissolving indium nitrate hydrate ([In(NO₃)₂·nH₂O], Sigma-Aldrich) and lanthanide nitrate hydrate ([La(NO₃)₂·nH₂O], [Ce(NO₃)₂·nH₂O], [Pr(NO₃)₂·nH₂O], [Nd(NO₃)₂·nH₂O], [Sm(NO₃)₂·nH₂O], [Eu(NO₃)₂·nH₂O], [Gd(NO₃)₂·nH₂O], [ Tb(NO₃)₂·nH₂O], [ Dy(NO₃)₂·nH₂O], [ Ho(NO₃)₂·nH₂O], [ Er(NO₃)₂·nH₂O], [Tm(NO₃)₂·nH₂O], [Yb(NO₃)₂·nH₂O], (Lu(NO₃)₂·nH₂O), (AlNd)₂₃O₃] in deionized water, which was optimized to the total concentration of metal ion of 0.2 M and In/Ln molar ratio of 19:1. All the precursor solutions were stirred vigorously for 12 h at room temperature and filtered through a 0.22 μm syringe filter before spin-coating.

Devices fabrication. A bottom-gate and top-contact source-drain electrode structure was used to fabricate In_{2}O_{3} TFT. Firstly a 200-nm thickness Al_{2}O_{3}:Nd gate dielectric layer with a capacitance density of 38 nF cm⁻² was formed by anodization on the surface of a 300-nm thick AlN/Al alloy film deposited on glass by sputtering and patterned by wet etch, which the details process have been reported in our previous report. Then, the substrates were cleaned ultrasonically in deionized water and isopropanol for 10 min, respectively, and dried in an air oven of 80 °C. Next, an ultraviolet light irradiating of a long time was used to treat a part (channel area) of the Al_{2}O_{3}:Nd surface with a stencil shadow mask, for the formation of a hydrophilic surface in the channel area. The Ln:In_{2}O_{3} precursor films were deposited in the wettable area irradiated by UV by spin-coating Ln:In_{2}O_{3} precursor solutions at 2000 rpm for 5 s and 6500 rpm for 40 s, followed by drying at 40 °C and thermal annealing at 300/350 °C for 1 h in an air condition. Finally, the Al source and drain electrodes were deposited on the Ln: In_{2}O_{3} layer by thermal evaporation, defined the channel area with 1000 μm width and 300 μm length by using a stencil shadow mask.

Devices characterization. The electrical characteristics of undoped In_{2}O_{3} and Ln:In_{2}O_{3} TFTs were measured using a semiconductor parameter analyzer system (Agilent B1500A) in conjunction with a probe station (Lakeshore CRX-VF) at room temperature and air condition. The NBIS stability was tested by monitoring evolutions of the transfer curves of MO TFTs based on a series of Ln incorporated In_{2}O_{3} semiconductors as a function of the stress time under gate bias stresses of −20 V combining with white LED irradiation of optical density of 250 Lux, respectively. The energy levels of the functional layer were measured with Ultra-violet Photoelectron Spectrometer (UPS) of K-ALPHA⁺ of Thermo Fisher Scientific. The absorption spectrum was measured by using UV-2600. The enhanced photoluminescence spectra was measured by using FLS1000. The x-ray Photoelectron Spectroscopy (XPS) was measured by using K-ALPHA⁺ of Thermo Fisher Scientific with Mono AlKα. The carrier mobility for the saturation regime was calculated using:

\[ \mu = \frac{W/C}{\Delta L} (V_{GS} - V_{th})^2 \]

where \( \mu \) is the field-effect mobility, \( C \) is the areal capacitance per area of the gate dielectric, \( V_{th} \) is the threshold voltage, \( W \) is the channel width, and \( L \) is the channel length.

Data availability
The data that support the plots within this paper and other findings of this study are available from the corresponding authors upon reasonable request.

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Author contributions
L.F.L., P.H.H., and J.B.P. presented the idea and designed the experiment. P.H.H., C.C.D., and X.L. fabricated the devices. Y.B.W. and S.T.C. performed XPS measurements. Y.L.L. performed XRD measurements. P.H.H., C.H.D. carried out NBIS and PBIS measurements. M.X. and H.X. carried out NBTS and PBTS measurements. P.H.H. and L.F.L. wrote this manuscript. All authors participated in interpretation of the results and manuscript preparation.

Competing interests
The authors declare no competing interests.

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