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In-gap States of an a-IGZO Thin Film Studied via High-Sensitivity UV Photoemission Spectroscopy Using Low-Energy Photons

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Low-density electronic states in the energy gap of an amorphous In-Ga-Zn-O (a-IGZO) film control device performance. Herein, density of states (DOS) distribution from valence band to the in-gap states of 10^{14}cm^{-3}eV^{-1} level was determined using high-sensitivity UV photoemission spectroscopy (HS-UPS). Exponential tail states accompanying two energetically-localized states were directly observed as reported previously. The observed slope of the exponential tail state was different from the Urbach energy derived using photothermal deflection spectroscopy, indicating the importance of directly observing the DOS of in-gap states.

Amorphous In-Ga-Zn-O (a-IGZO) is a transparent semiconductor that has attracted attention over the years. It has high field mobility, high transparency due to a wide gap, and small threshold voltage swing.[1)] Therefore, it will likely replace the traditional material, a-Si:H, as the channel material for thin-film transistors (TFTs) in flat panel displays. However stability and reliability problem exist due to the in-gap states in the energy gap. Therefore understanding and controlling the in-gap states are essential for improving device performance.

Intensive studies on the in-gap states of a-IGZO have been reported in relation to bias and light-induced stress;[2)] for example, threshold voltage ($V_{\rm th}$) tends to shift positively after positive gate bias stress (BS) because negative carriers are trapped on an interface with a dielectric layer or injected into the dielectric from the a-IGZO channel.[3)] However, $V_{\rm th}$ shifts negatively under negative bias illumination stress (NBIS) because light illumination induces

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occupied deep in-gap states derived from oxygen defects (V_O) to be ionized ($V_O \rightarrow V_O^+ + e^-$ or $V_O^{2+} + 2e^-$).[1),4),5),6)] Another possibility is that holes induced by light can be captured by occupying the in-gap states.[7),8)] This important stability issue under NBIS is yet to be understood whereas the stability problem under BS for annealed TFTs has been almost solved by passivating layers.[1)]

The in-gap states of inorganic semiconductors can be classified into two types; the *tail state* whose density of states (DOS: $D(E)$) can be expressed as an exponential function of energy E ($D(E) \propto \exp(-E/E_0)$) and the energetically-localized states whose DOS can be described as a Gaussian. The nature and origin of these two types of in-gap states have been actively discussed in the literature. Yu *et al*. proposed the DOS distribution in the entire band gap region by combining results from multiple experiments[9)] and theoretical calculation in the literature.[10)] In the model, the DOS of occupied tail states was derived by substituting the Urbach energy (E_u) for the exponential slope (E_0). The occupied localized states derived from V_O located 1 eV above the valence band maximum (VBM) were estimated using the first-principles calculation.[10)] Moreover, the DOS curve obtained from multi-frequency capacitance-voltage (CV) measurements was assigned to the empty in-gap states. Similar studies have evaluated the DOS based on results from optical absorption spectroscopy, electrical measurements, and device simulations.[2),6),11),12),13)]

In these studies, some problems associated with investigating the DOS in the energy gap still exit. The first is how to evaluate the exponential slope of tail states. In principle, it is expected that E_u should not equal E_0 because the absorption coefficient depends on the joint DOS; the exponential behavior in the pre-edge region of the absorption spectrum reflects the transition from the occupied tail state to the conduction band and also the transition from the valence band to the unoccupied tails state. Thus, the possible error of substituting E_u for E_0 should be examined. The second point is that the DOS has been observed using indirect methods. Electrical measurements and device simulations need to assume some models to derive the DOS, and final results depend on the model used; thus, directly deducing an accurate in-gap DOS is challenging.[1),14)] Moreover, optical and trap spectroscopies determine the relative energy location among the in-gap states, valence band and conduction band. However, the absolute energy position relative to the vacuum or Fermi levels cannot be easily determined.

Photoemission spectroscopy (PES) is a common method to probe the occupied DOS of materials. This method can directly evaluate the DOS with few assumptions, and, the absolute energy position of occupied states can be determined relative to vacuum and Fermi levels. By

analyzing the angular or photon energy dependence of spectra, the nature of the initial state wave function can be evaluated. However, the application of PES to investigate in-gap states has been limited, notwithstanding its merits.

Recently hard X-ray photoemission spectroscopy (HAX-PES) has been applied to a-IGZO.[15),16)] The bulk electronic structure including the in-gap states was observed using the synchrotron radiation (SR) light source of high photon energy and flux for longer probing depth. The photoionization crosssection depends on the element and photon energy. In HAX-PES, in-gap states due to valence s-states of In, Ga, and Zn atoms are enhanced, but the oxygen 2p state is missing because of the small crosssection.[17)] To understand the DOS of in-gap states, measurement using UV photoemission spectroscopy (UPS), which is sensitive to light elements such as oxygen, is desired. Further, the detection limit of HAX-PES is limited to approximately 10^{19} $eV^{-1}cm^{-3}$ level.[1)] Similar to NBIS, exposure to strong light such as a hard X-ray from SR may induce some damage to the sample. In the HAX-PES work, the formation of metastable states near the Fermi level is reported and can be related to light illumination;[15),16)] therefore, to complement the HAX-PES work, high-sensitivity UPS measurement with low photon energy and flux is necessary.

In the present study, we applied high-sensitivity UPS (HS-UPS) to an a-IGZO film to investigate the DOS of occupied in-gap states. Recently, the detection limit of PES improved using a monochromatized light source and low noise detector.[18)] We developed this HS-UPS method using an energy-tunable light source with extremely low stray light to enable the detection of weak in-gap states to the level of 10^{15} $eV^{-1}cm^{-3}$ or less for organic materials.[19,20)] The bulk-sensitive measurement is possible because of the long probing depth caused by the usage of deep UV light.[21)] In our method, a series of spectra of various excitation photon energy $h\nu$ was recorded, and connected by adjusting the difference in photoionization crosssection for different $h\nu$ to estimate the DOS of the sample material. The so-called "overlap method" was used for the adjustment based on the assumption that the spectral intensity is dependent on the $h\nu$ but the line shape is invariant irrespective of the $h\nu$. In this study, as another adjustment method, the constant final state method (CFS) was applied. Yield spectroscopy using the CFS method has been used to detect in-gap states in some inorganic semiconductors.[22),23)] We applied this scheme to HS-UPS to estimate more reliable DOS. Regarding the relation between E_0 and E_u, we measured photothermal deflection spectroscopy (PDS) with high sensitivity to determine the E_u. The value of E_0 obtained from HS-UPS was compared to the observed value of E_u to discuss the validity of substituting E_u for E_0.

a-IGZO thin films (In:Ga:Zn ~ 1:1:1) were deposited on n-doped Si wafer and quartz

substrate using a load-lock DC magnetron sputtering system (ULVAC: CS200) under the conditions of 2×10^{-4} Pa base pressure and 0.5 Pa sputtering pressure. The ratio of oxygen gas (O_2/(Ar + O_2)) was 10 vol.%. The samples were heat-treated in a warm air dryer at 23°C and 50% and stored in a desiccator under nitrogen atmosphere before the measurement.

The HS-UPS measurements were performed at Chiba University using a homemade system.[19] Pure excitation light with low stray light (10^{-9} at 632 nm) was obtained using a zero-dispersion double monochromator (Bunko Keiki: BIP-M25-GTM). An electrostatic hemisphere analyzer (PSP: RESOLVE 120) was used to detect photoelectrons along the surface normal direction. For the normal UPS measurement, a helium discharge lamp (Omicron HIS13), which emits HeI resonance line (hν = 21.22 eV), was used. The details of the measurement were described in a previous study.[19]

The PDS measurement was performed at University of Cambridge. 50 nm thick a-IGZO film was prepared on a quartz substrate as the sample. Photon absorption by the sample was detected as a refractive index gradient in the area surrounding the sample surface. By immersing the sample in an inert liquid FC-72 Fluorinert (3M Company) with a high refractive index change due to temperature, photoabsorption can be detected with high-sensitivity. The details were described in a previous study.[24]

Figure 1 shows the absorption spectra of the a-IGZO film measured using ellipsometry and PDS methods. The two spectra were connected by overlapping them around hν = 3 – 3.2 eV region to normalize the spectral intensity. As shown in Fig.1(a), the Tauc band gap energy was 3.19 eV. In Fig.1(b), the absorption spectrum is plotted on semilog scale; two linear regions were observed at hν = 2 – 2.6 and 2.6 – 3.0 eV. The latter linear region was assigned as the Urbach tail with a value of 110 meV for E_u. This value of E_u is consistent with those reported in the literature (110,[9] 124,[25] 160 meV[10]).

Figure 2(a) shows a conventional HeI UPS spectrum. The horizontal axis is the electron binding energy relative to the Fermi level, which was determined by measuring a gold film. The vertical axis is the intensity of the photoelectrons on the linear scale. The broad structure due to the valence band was observed at 3-9 eV, and the VBM was determined as 3.16 eV from the observed onset. This spectral feature was consistent with previous reports.[26),27] In the spectrum, another onset-like structure was also observed at 3.75 eV. Considering the Tauc band gap of 3.19 eV, the assumption of VBM at 3.75 eV led to an unrealistic situation in which the conduction band minimum (CBM) was located below the Fermi level. Thus, VBM position was determined at 3.16 eV, which indicated that the location of the CBM was close to the Fermi level. The weak onset structure at 3.16 eV can be related to the band structure in

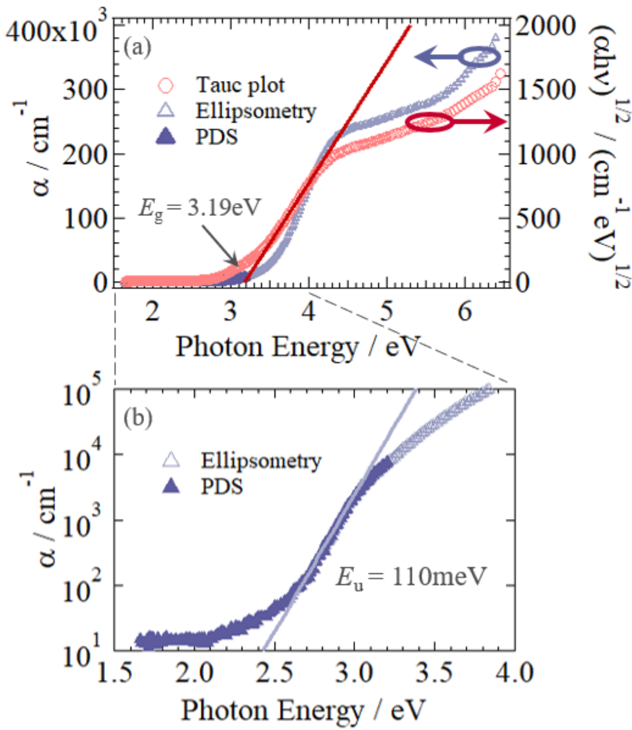

Fig. 1. (a)Absorption spectra of an a-IGZO film constructed using ellipsometry (blue open triangle) and PDS (blue solid triangle) methods. The value of $\sqrt{\alpha h\nu}$ was plotted at the right axis as the Tauc plot. (b)Magnification of the spectra in the low hν region on semilog scale.

which the VBM is not located at the Γ point as suggested by theoretical calculation.[28] The photoelectron emission from the VBM may be relatively weakened because the spectra were measured in normal emission geometry in this work.

The low energy region above the VBM in the HeI spectrum was noisy (not shown), and it was not enough to observe the gap states. However, the HS-UPS spectrum measured using hν=7.7 eV light had a clear structure in the gap region. In this method, the UPS spectra were obtained by changing the value of the hν by 0.1 eV. A series of the spectra for hν =4.7 to 8.8 eV is shown in Fig.2(b), indicating that the structure due to gap states extends to the Fermi level. No photoelectron was detected for hν $<$ 4.7 eV. The spectral shift during the measurements was less than 0.1 eV, suggesting that the artificial defects such as sample damage, charging, or photo-voltaic shift can be excluded.

Figure 3(a) shows all the HS-UPS spectra for hν = 4.7 to 8.8 eV whose intensities were normalized by photon flux. To quantitatively evaluate the DOS in the gap states from these spectra, the intensity of each HS-UPS spectrum for hν = 4.7 - 8.8 eV should be normalized because the probability of photoelectron emission depends on the hν.

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60

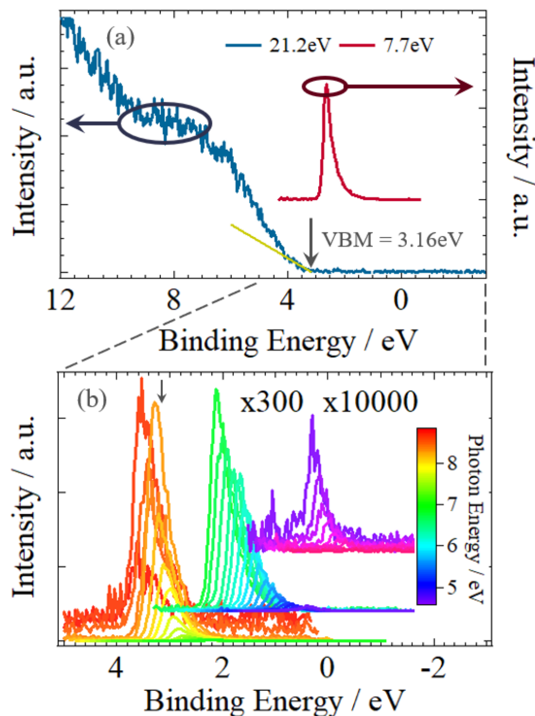

Fig. 2. (a) HeI (hν = 21.22 eV) UPS spectrum of a-IGZO thin film (blue line) with that for hν = 7.7 eV(red line) in the scale of electron binding energy relative to the Fermi level. (b) The series of HS-UPS spectra for hν = 4.7 - 8.8 eV. The values of hν are displayed in the color rainbow bar.

According to the *three-step model*,[29)] the photoemission intensity from the electron with the binding energy E_B by a photon of hν, $N(\mathrm{h}\nu, E_\mathrm{B})$ can be expressed as

$$N(\mathrm{h}\nu, E_\mathrm{B}) \propto (\mathrm{h}\nu)|M_\mathrm{fi}(\mathrm{h}\nu, E_\mathrm{B})|^2 D_\mathrm{i}(E_\mathrm{B}) D_\mathrm{f}(\mathrm{h}\nu - E_\mathrm{B}) X(\mathrm{h}\nu - E_\mathrm{B}) T(\mathrm{h}\nu - E_\mathrm{B}). \quad (1)$$

Where $|M_\mathrm{fi}|$, D_i, D_f, X, and T are the transition element from initial to final states, DOS of the initial state, DOS of the final state, transmission probability, and surface escape function, respectively. In our previous study, the *overlap method* was proposed to normalize the spectra. In the method, $N(\mathrm{h}\nu, E_\mathrm{B})$ is simplified to $\sigma(\mathrm{h}\nu)D_\mathrm{i}(E_\mathrm{B})$, where photoionization crosssection σ is assumed to depend on only hν. This lack of the terms D, X and T indicates that the spectral line shape is invariant, and the intensity changes with hν. The DOS can be approximated by overlapping the spectral part with similar line shape between adjacent photon energy spectra to eliminate the photon energy dependence. The DOS curve derived using the overlap method was connected to the HeI spectrum, and plotted as an orange triangle in Fig.3(a). The line shape of the DOS in the gap region was linear, and energetically-localized gap (peak or shoulder structures), which is often reported in the literature, was not observed. The missing of the localized state was due to the assumption of invariant line shape in the overlap method.

Thus, the concept of the *CFS method* was introduced to improve the normalization. In this method, the photoemission intensity at fixed kinetic energy ($E_{\mathrm{k}}^{\mathrm{fix}}$) is plotted as a function of hν. This implies that the final state is fixed to $E_{\mathrm{k}}^{\mathrm{fix}}$, rendering D_{f}, X, T constant in Eq.1. Thus, CFS spectrum intensity for E_{B} (N_{CFS}) constructed from hν-HS-UPS is expressed as

$$N_{\mathrm{CFS}}(E_{\mathrm{B}}) \propto (\mathrm{h}\nu)|M_{\mathrm{fi}}(\mathrm{h}\nu, E_{\mathrm{B}})|^2 D_{\mathrm{i}}(E_{\mathrm{B}}). \qquad (2)$$

To deduce the DOS of the initial state, the information of $M_{\mathrm{fi}}(\mathrm{h}\nu)$ is necessary. This CFS method has been applied as yield spectroscopy to investigate the gap states of inorganic semiconductors,[22),23)] but the details of the dependence of M_{fi} are not established. Regarding silicon, Jackson et al. proposed that $|M_{\mathrm{fi}}|^2 \propto (\mathrm{h}\nu)^{-5}$.[30)] Here we proceeded with the CFS normalization for a-IGZO by assuming the same hν dependence as silicon. The relative D_i curve was obtained by setting $E_{\mathrm{k}}^{\mathrm{fix}} = 0.25$ eV($E_{\mathrm{B}} = 5.14$ eV) which corresponded to the peak position of the secondary electrons. The curve was connected to the HeI spectrum and plotted as a red circle in Fig.3(a). The absolute value of DOS was deduced by comparison with the theoretical DOS:[31)] our relative D_i curve was normalized to match the integrated density of the valence band structure (from VBM to 8 eV) for the theoretical calculation. The obtained D_i is plotted in Fig.3(b). Now the D_i curve has a tail state and additional structures. Notably, the $10^{14}\mathrm{cm}^{-3}\mathrm{eV}^{-1}$ level density was also detected using our HS-UPS method.

To analyze the in-gap states, we performed curve-fitting by assuming a linear combination of the exponential tail state and two Gaussian-type localized states. The fitting result is plotted in Fig.3(b); the exponential tail state slope, E_0, was 207 meV and the peak density and energy of the two Gaussian were $2.89 \times 10^{18}\mathrm{cm}^{-3}$, 1.86 eV (localized state 1), and $1.62 \times 10^{17}\mathrm{cm}^{-3}$, 1.26 eV (localized state 2), respectively.

Further, we compared the CFS results with the literature. Regarding the tail state slope, E_0, the value in this work is 207 meV, and is twice that of the observed value E_{u} (110 meV in the present study). This result indicates that the substitution of E_{u} for E_0 is not a good approximation to evaluate E_0. We compared the two observed Gaussian-like states with theoretical works. A DFT calculation reported that localized oxygen defect states are above the VBM,[10)] which corresponds to the localized state 1. Other theoretical studies have revealed that oxygen defects are localized at different positions, depending on the surrounding local environment.[31),32)] Judging from the energy position, the origin of the localized states 1 and 2 can be related to these oxygen defects group ($\mathrm{V_O}$). Irrespective of the exact origin of the gap states, the observation of the two localized states in our HS-UPS strongly suggests that the wavefunction of these states has O 2p character to some extent, because the O 2p

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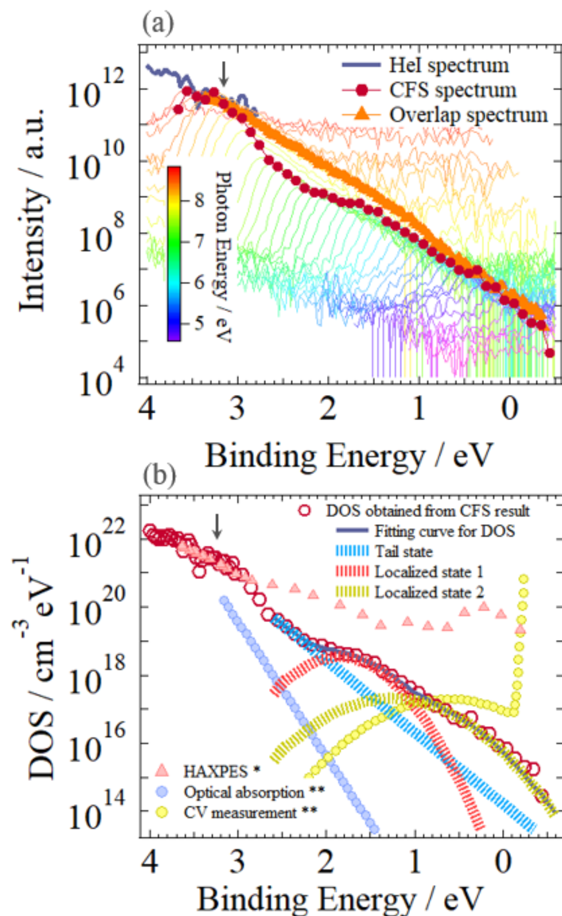

Fig. 3. (a)All hν-HS-UPS spectra (hν = 4.7 - 8.8 eV) are displayed on log scale. DOS curves estimated by *overlap* and *CFS* methods are shown by the orange triangle and red circle, respectively. The *overlap* spectrum showed only tail states, but the *CFS* spectrum exhibited additional structures.(b)The result of peak-fitting of CFS spectrum compared with HAX-PES(*),[16] optical absorption and CV measurement(**).[9] The position of VBM is marked by the arrow.

photoionization crosssection is larger than those for In, Ga, and Zn valence atomic orbitals for low photon energy. Such contribution of O 2p state is consistent with the calculation of ref.[10] in which the in-gap states above the VBM for oxygen deficient a-IGZO mainly comprised O and Zn atomic orbitals. From HAX-PES, sub gap states have been observed as shown by triangles in Fig.3(b).[15][16] One is near-VBM states around 2 eV, the other is near-CBM-states close to the Fermi level. In the references, the density of near-VBM states is estimated to be $7.1 \times 10^{20} cm^{-3}$ for the deposited sample. The value is considerably larger than our result because of the difference in photoionization crosssection. The density of the near-VBM state is estimated relative to the photoemission intensity from the valence band. The main component of VB is O 2p orbital, and its photoionization crosssection is smaller for higher

hν photon, making the VB structure smaller.[17] The estimated density of near-VBM states was overestimated if the character of the wave function of the near-VBM state was different from that of the VB. The reverse situation is expected for the case using lower hν; the density of the near-VBM states might have been underestimated in this study. From the point of hν dependence on photoionization crosssection, HS-UPS using low energy hν is complimentary to HAX-PES using higher hν. However, if our approximation of $|M_{fi}|^2 \propto \mathrm{h}\nu^{-5}$ in ref.[30] is not bad for a-IGZO, our estimated DOS value is plausible. In ref,[9] the density of the localized state determined using multi-frequency CV measurement was in the order of $10^{17}\mathrm{cm}^{-3}\mathrm{eV}^{-1}$, which is close to the density of the localized state 2 in this study, confirming the validity of our method. Regarding near-CBM state in HAX-PES, no corresponding structure was observed in the HS-UPS. This discrepancy can be ascribed to two possible reasons: (i)near-CBM state due to In 5s is missing in HS-UPS because of small photoionization crosssection, and (ii)near-CBM structure may be due to irradiation damage by strong excitation light from SR for HAX-PES measurement.

In summary, we conducted HS-UPS measurement to investigate the DOS of the gap states of a-IGZO. The DOS of a-IGZO from the valence band to $10^{14}\mathrm{cm}^{-3}\mathrm{eV}^{-1}$ level weak gap states was determined using CFS method. The slope of the exponential tail states was determined to be approximately 200 meV, which cannot be substituted by the Urbach energy. Two Gaussian-like localized states, which can be assigned as oxygen defect states, were observed. These results demonstrates that the HS-UPS is a powerful tool to directly investigate the DOS of gap states. To clarify the absolute density of gap states, photoemission spectroscopy using both low and high photon energies is desired.

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