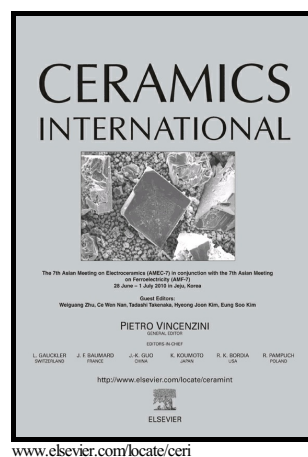# Author's Accepted Manuscript

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Phase-controlled SnO₂ and SnO Growth by Atomic Layer Deposition using

Bis(*N*-ethoxy-2,2-dimethyl propanamido)tin Precursor

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Abstract

Atomic layer deposition (ALD) of SnO and SnO_2 thin films was successfully demonstrated over a wide temperature range of 70–300 °C using a divalent Sn-precursor, bis(N-ethoxy-2,2-dimethyl propanamido)tin ($Sn(edpa)_2$). The regulated growth of the SnO_2 and SnO films was realized by employing O_2-plasma and H_2O, respectively. Pure SnO_2 and SnO films were deposited with negligible C and N contents at all the growth temperatures, and the films exhibited polycrystalline and amorphous structures, respectively. The SnO_2 films presented a high transmittance of > 85% in the wavelength range of 400–700 nm and an indirect band gap of 3.6–4.0 eV; meanwhile, the SnO films exhibited a lower transmittance of > 60% and an indirect band gap of 2.9–3.0 eV. The SnO_2 films exhibited n-type semiconducting characteristics with carrier concentrations of 8.5×10^{16}–1.2×10^{20} cm^{-3} and Hall mobilities of 2–26 cm^2/V·s. By employing an alternate ALD growth of SnO and SnO_2 films, SnO_2/SnO multilayer structures were successfully fabricated at 120 °C. The in-situ quadrupole mass spectrometry analysis performed during ALD revealed that the oxidation of chemisorbed Sn-precursor occurs dominantly during the $Sn(edpa)_2$/O_2-plasma ALD process, resulting in the production of combustion by-products, whereas the $Sn(edpa)_2$/H_2O ALD process was governed by a ligand exchange reaction with the maintenance of the original oxidation state of Sn^{2+}.

Introduction

Binary oxide semiconductors of the Sn–O system, such as SnO_2 and SnO, have been extensively investigated owing to their versatile applications in displays [1-3], gas sensors [4,5], photocatalysts [6,7], transparent electronics [8,9], and optoelectronics [10,11]. Owing to the different oxidation states (+4 and +2) of the Sn cation, the SnO_2 and SnO films exhibit distinctive optical, chemical, and electrical properties. SnO_2 is an n-type semiconducting oxide with an electron concentration level of 10^{18}–10^{21} cm^{-3}, and the formation of excess electrons is attributed to the presence of intrinsic point defects such as the oxygen vacancy or Sn interstitial in SnO_2 [12-14]. The largely overlapped spherical 5s orbitals in SnO_2 enables the facile transport of electrons in the conduction band, resulting in properties exhibiting high potential, including a high electron mobility and low resistivity [14]. Meanwhile, SnO generally exhibits a p-type semiconductor nature owing to the presence of intrinsic Sn vacancies or oxygen interstitials. First-principle calculations revealed that Sn vacancies mainly contribute to hole conduction by forming unoccupied states near the valence band maximum [15,16]. Owing to its remarkable hole transport property, a high field effect mobility of 0.13–6.75 $cm^2/V·s$ has been achieved from SnO-based p-channel thin film transistors (TFTs) [3,17-19].

Recently, as the demand for realizing complementary circuit devices based on oxide semiconductors has increased, the growth processes of n-type SnO_2 films as well as p-type SnO films have received significant attention. The growth of n-type SnO_2 film has been extensively conducted using various vacuum deposition processes such as sputtering [20], evaporation [21], chemical vapor deposition [22,23], and atomic layer deposition (ALD) [24-30]. Among these methods, ALD exhibits superior advantages for producing physically and chemically uniform films on large and complex substrates owing to its unique self-limiting deposition behavior. For

decades, various combinations of Sn-precursor and reactant have been explored for performing ALD of SnO_2. Sn-halides such as $SnCl_4$ and SnI_4 were used for producing highly pure polycrystalline SnO_2 films; however, high deposition temperatures in the range of 300–750 °C are required owing to the insufficient reactivity of Sn-halide precursors [24,25]. In addition, Sn-halide precursors form corrosive by-products such as HCl, which deteriorates the resultant film properties. Meanwhile, the adoption of metal–organic Sn-precursors for ALD of SnO_2 enabled the growth of high-quality SnO_2 films at relatively lower deposition temperatures (< 300 °C). Tetrakis(dimethylamido)tin(IV) (TDMASn) has been commonly used for producing SnO_2 films by ALD, and the use of different reactants such as H_2O, H_2O_2, and O_3 has been explored [26-28]. ALD using TDMASn/H_2O resulted in SnO_2 film with a growth rate of 0.06–0.07 nm/cycle at 100–200 °C, whereas the use of TDMASn/O_3 and TDMASn/H_2O_2 resulted in enhanced SnO_2 growth rates of 0.09–0.13 nm/cycle owing to the higher reactivity of H_2O_2 and O_3 compared to H_2O. Regardless of the reactant type, n-type SnO_2 films were obtained from TDMASn. Dibutyl-tin(IV)-diacetate (DBTA) and tin(IV)-butoxide were used as Sn-precursors in the plasma-enhanced ALD (PEALD) process at deposition temperatures of 200–400 °C to obtain pure SnO_2 films suitable for gas sensor and Li-ion battery applications [29,30].

In contrast to n-type SnO_2, very limited success has been achieved in the fabrication of p-type SnO and its applications. Most of the studies on the growth of SnO film employed physical vapor deposition (PVD) methods such as reactive sputtering and reactive evaporation under delicately regulated process conditions with respect to the process pressure, partial pressure of oxidative or reductive gases, and deposition temperature [17,31]. This is because SnO is metastable and can be straightforwardly oxidized to SnO_2 or decomposed to SnO_2 and Sn metal by a disproportionation reaction [32]. Therefore, an alternate method for producing pure SnO films with a wide and stable process window should be developed. We reported the successful growth of pure SnO for the first time by ALD using bis(dimethylamino-2-methyl-2-propoxy)tin(II) (Sn(dmamp)$_2$) and H_2O [33]. Polycrystalline SnO films exhibiting p-type

conductivity were obtained at 150–210 °C. Furthermore, the ALD-grown SnO film obtained from Sn(dmamp)$_2$/H$_2$O exhibited remarkable p-channel TFT performances with a high field effect mobility of ~1 cm^2/V·s and I$_{on}$/I$_{off}$ ratio of ~2 × 10^6 [34].

In this study, we conducted ALD growth of SnO$_2$ and SnO films using an Sn-precursor, bis(*N*-ethoxy-2,2-dimethyl propanamido)tin (Sn(edpa)$_2$); moreover, the phase of the SnO$_x$ films, SnO$_2$ and SnO, was effectively controlled by employing different reactants, namely, O$_2$-plasma and H$_2$O, respectively. The surface reactions during the SnO$_2$ and SnO ALD processes were investigated by employing in-situ mass spectrometric residual gas analysis. Furthermore, ex-situ analyses on the chemical, physical, optical, and electrical properties as well as microstructures of the SnO$_2$ and SnO films were performed.

Experimental Section

ALD of SnO$_2$ and SnO was carried out in a 4-inch showerhead type reactor (ForALL, Korea) on Si and quartz substrates at deposition temperatures within 70–300 °C. The base pressure and process pressure during the ALD process were 20 mTorr and 1–1.5 Torr, respectively. The Sn(edpa)$_2$ precursor was synthesized on labscale and employed for growing both SnO$_2$ and SnO films. As shown in Fig. S1a, Sn(edpa)$_2$ is a homoleptic metal-organic complex with the central Sn(II) atom tetra-coordinated by two edpa chelating ligands. As two of the four neighboring oxygen atoms form ionic bonds with the central atom and the others form coordinate bonds, Sn(edpa)$_2$ exhibits divalent rather than tetravalent characteristics. The detailed synthetic procedure and characteristics of Sn(edpa)$_2$ have been reported previously [35]. During ALD, Sn(edpa)$_2$ was kept in a canister at 60 °C and delivered into the reactor with an Ar carrier gas flow of 100 standard cubic centimeters per minute (sccm). The precursor delivery line was heated to 75 °C during the deposition process. For fabricating the SnO$_2$ and SnO films, O$_2$-plasma and H$_2$O, respectively, were introduced as reactants. O$_2$-plasma was generated with an

oxygen flow of 100 sccm at the plasma power of 100 W. The canister for H_2O was maintained at 25 °C, and the H_2O vapor was introduced into the chamber without any carrier gas. A cycle of the ALD process consisted of four sequential steps; (1) $Sn(edpa)_2$ pulse, (2) Ar purge (500 sccm), (3) reactant gas pulse (O_2-plasma or H_2O), and (4) Ar purge (500 sccm). To remove the excess Sn-precursor and reactant as well as by-products, Ar purge gas was introduced for 10 s and 15 s for the O_2-plasma- and H_2O-based process, respectively.

The thickness, refractive index, and extinction coefficient (k) of the ALD deposited SnO_2 and SnO films were measured by spectroscopic ellipsometry in the wavelength range of 275–826 nm (SE, Horiba scientific, UVISEL). The chemical binding properties and O/Sn composition ratios of the SnO_2 and SnO films were examined using X-ray photoelectron spectroscopy (XPS, Thermo Scientific, K-alpha) with Al Kα monochromatic X-ray source. The photoelectrons were collected at an analyzer pass energy of 50 eV and a photoelectron take-off angle of 0°. For XPS depth profile analysis, the deposited films were sputtered with an Ar^+ ion beam at 2 keV. The Avantage software was used for spectral deconvolution and depth profiling. To reveal the crystallinity of the SnO_2 and SnO films, glancing angle X-ray diffraction (GAXRD, Rigaku, smartlab) was employed at the incident X-ray angle of 1°. The topography of the SnO_x film surfaces was measured by atomic force microscopy (AFM, DI-3100, Veeco). Atomic-scale crystallographic examinations of the SnO_2/SnO multilayer structure fabricated on the TiN substrate were performed using high-resolution transmission electron microscopy (HRTEM, JEM-2100F, JEOL LTD.). The transmittance of the films in visible light was measured using UV−Vis spectroscopy (Shimadzu, UV-1800). The electrical properties of the deposited films were examined using Hall measurements.

For in-situ analysis of the surface chemical reaction during the SnO_2 and SnO ALD processes, a quadrupole mass spectrometer (QMS, Balzers, ABB Extrel MEXM-1000) was connected to the deposition system. The reaction by-products were collected through the capillary line and

ionized by electron bombardment at 1 KeV. The time-resolved by-product signals with different mass-to-charge ratios (m/z) of 30, 44, 57, and 146 corresponding to NO, CO_2, ^tBu, and edpaH, respectively, were detected using a secondary electron multiplier.

Results and Discussion

The self-limited reaction of the $Sn(edpa)_2$/O_2-plasma and $Sn(edpa)_2$/H_2O ALD processes was examined at a growth temperature of 120 °C by increasing the Sn-precursor and reactant pulse times. As shown in Fig. 1a, the $Sn(edpa)_2$/O_2-plasma PEALD process exhibited a saturated growth behavior at $Sn(edpa)_2$ and O_2-plasma pulse-lengths of over 10 and 5 s, respectively. A saturated growth rate of ~0.07 nm/cycle was achieved, which is comparable to that obtained for TDMASn/H_2O ALD [26,27]. For $Sn(edpa)_2$/H_2O, a self-saturated surface reaction occurred with $Sn(edpa)_2$ and H_2O pulse lengths of over 10 and 1 s, respectively (Fig. 1b). As compared to the $Sn(edpa)_2$/O_2-plasma process, a significantly lower growth rate of 0.026 nm/cycle was obtained for the $Sn(edpa)_2$/H_2O process; this may be ascribed to the lower reactivity of H_2O. The change in the growth rate achieved with both the ALD processes as a function of the deposition temperature was examined in the growth temperature range of 70–300 °C (Fig. 1c). The SnO_2 and SnO ALD processes were conducted at various temperatures with fixed pulse conditions of 12 s (Sn-precursor)–10 s (Ar purge)–5 s (O_2-plasma)–5 s (Ar purge) and 12 s (Sn-precursor)–15 s (Ar purge)–2 s (H_2O)–5 s (Ar purge), respectively. For the $Sn(edpa)_2$/O_2-plasma PEALD process, a constant growth rate of 0.07 nm/cycle was achieved at the ALD temperature window of 70–180 °C. Above 180 °C, the growth rate increased with an increase in the deposition temperature. This increase in the growth rate may be ascribed to the limited thermal stability of the $Sn(edpa)_2$ precursor. The thermal stability of the $Sn(edpa)_2$ precursor was examined by introducing only the Sn-precursor into the reactor at elevated stage temperatures of 90–300 °C (Fig. S1b). The Sn layer density on the Si substrate examined by XRF started to increase rapidly

from 180 °C, indicating the onset of thermal decomposition of $Sn(edpa)_2$. The NMR spectra of the $Sn(edpa)_2$ precursor exhibit results consistent with those obtained by XRF (Fig. S1c). As compared to the NMR spectrum of pristine $Sn(edpa)_2$, a different NMR spectrum was obtained when $Sn(edpa)_2$ was maintained at a high temperature of 200 °C for 1 d. This is likely to be owing to the thermal decomposition of $Sn(edpa)_2$ occurring at approximately 200 °C. The $Sn(edpa)_2/H_2O$ ALD process exhibited an almost constant growth rate of 0.026 nm/cycle at all the investigated temperatures (70–300 °C) notwithstanding the limited thermal stability of $Sn(edpa)_2$ above 200 °C. The discrepancy in the temperature dependence of the growth rate between the $Sn(edpa)_2/O_2$-plasma and $Sn(edpa)_2/H_2O$ processes may be attributed to the formation of different surface species after the O_2-plasma and H_2O pulse steps. Generally, in the O_2-plasma-assisted PEALD, both surface hydroxyl and carbonate groups are formed as reactive sites for the chemisorption of incoming metal-precursors, whereas the H_2O-based ALD process predominantly generates surface OH groups [36]. Accordingly, it is presumed that the rapid increase in the growth rate in the $Sn(edpa)_2/O_2$-plasma PEALD process over 200 °C is owing to the higher reactivity of the partially decomposed Sn-precursor with the carbonate surface groups than with the OH surface. The refractive indexes of the resultant SnO_x films were measured by fitting the SE results using the Adachi–Forouhi dispersion model, as shown in Fig. 1d. Luo et al. reported a change in the refractive index of SnO_x films from 3.0 to 1.8 as the phase of the film varied from SnO to SnO_2 [37]. The refractive index (at a wavelength of 550 nm) of the films deposited by $Sn(edpa)_2/O_2$-plasma PEALD was 1.9–2.0 at all the deposition temperatures, which is reasonably consistent with that of the reported values for the SnO_2 films. However, the films grown with $Sn(edpa)_2/H_2O$ exhibited a higher refractive index of 2.7–2.8, which is close to that obtained for the SnO phase [37].

To further reveal the phase of the deposited SnO_x films and its chemical properties depending on the selection of the co-reactant, XPS surface and depth profiling analysis were conducted, as depicted in Figs. 2a–c. Figure 2a shows the normalized Sn 3d spectra for the SnO_x films

deposited using O_2-plasma or H_2O at different reactor temperatures. With Sn(edpa)$_2$/O_2-plasma, the Sn $3d_{5/2}$ spectra exhibited a peak centered at 486.7–486.8 eV irrespective of the growth temperatures, indicating the Sn oxidation state to be +4. The Sn $3d_{5/2}$ sub-peak corresponding to the Sn^{2+} chemical state (~486.2 eV) was not observed. This implies that Sn cation with an oxidation state of +2 in pristine Sn(edpa)$_2$ is completely converted to Sn^{4+} during the O_2-plasma-based PEALD process because of the strong oxidation power of O_2-plasma, resulting in the formation of the SnO_2 film. With the Sn(edpa)$_2$/H_2O process, the peak positions in the Sn $3d_{5/2}$ spectra shifted to marginally lower binding energy values of 486.2–486.3 eV irrespective of the deposition temperatures. This is ascribed to the formation of SnO by maintaining the original oxidation state of +2. The broader Sn $3d_{5/2}$ XP spectra width achieved for the SnO film is likely to have resulted from the marginal presence of the Sn^{4+} oxidation state, as evident from the weak sub-peaks observed at ~486.7 eV as well as the structural disorder of amorphous SnO. In addition, the O 1s XP spectra of the deposited were examined (Fig. S2). The O 1s XP spectra result is consistent with the Sn 3d XP spectra in that O-Sn^{4+} and O-Sn^{2+} binding states were formed using Sn(edpa)$_2$/O_2-plasma and Sn(edpa)$_2$/H_2O precursor combinations, respectively. The structural property of the deposited films will be discussed later. To examine the atomic composition profiles of the deposited films, the XPS depth profiling of the SnO_2 and SnO films grown at 120 °C was examined, and the results are shown in Figs. 2b and c, respectively. The SnO_2 film grown with the O_2-plasma-based PEALD exhibited an O/Sn ratio of 1.2 and a uniform O/Sn distribution in the depth direction. The SnO_2 films grown at 120 °C contained negligible C and N impurities. In contrast, the SnO film formed with H_2O as the reactant exhibited a significantly lower O/Sn ratio of 0.74. The significant difference between the O/Sn ratios of the films achieved with Sn(edpa)$_2$/O_2-plasma and Sn(edpa)$_2$/H_2O indicates the remarkable phase controllability of the SnO_x ALD processes carried out in this study. It should be noted that the absolute O/Sn ratio determined by XPS quantitative analysis is not very accurate even after considering the atomic sensitivity factors of each element. In Fig. 2c, the gradual decrease in the O/Sn ratio with the increase in the Ar sputtering time is because of the

preferential oxygen loss from SnO occurring during sputtering, rather than the non-uniform distributions of O and Sn. The XPS depth profiles of the SnO_x films deposited at the different temperatures are shown in Fig. S3. The O/Sn ratios as well as the impurity level of the SnO_2 and SnO films were not strongly affected by the growth temperature.

The crystallinity of the SnO_2 and SnO films grown on Si substrates was investigated by ex-situ GAXRD. Figure 3a shows the diffraction patterns of the SnO_2 films deposited at various temperatures within 70–300 °C. At a low temperature of $\geq$ 70 °C, the deposited films exhibited peaks corresponding to polycrystalline SnO_2, with the diffraction peaks observed at 26.6° [SnO_2 (110)], 33.9° [SnO_2 (101)], and 38.2° [SnO_2 (200)]. The growth of polycrystalline and pure SnO_2 below 100 °C appears to exhibit potential in terms of the application of temperature-damageable substrates such as plastics, textiles, and biomaterials. Within an ALD temperature window of 70–120 °C, a strong (101) preferred orientation was observed, whereas the films deposited at 220–300 °C exhibited a randomly oriented SnO_2 structure. At 70 and 120 °C, no other phase (e.g., metallic Sn, SnO, and SnO_{2-x}) were detected, indicating the formation of a pure SnO_2 film. Beyond the ALD temperature window of 220 and 300 °C, a diffraction peak was observed at 24.7°, which may be attributed to the oxygen deficient SnO_{2-x} phase [38]. The SnO films obtained from $Sn(edpa)_2/H_2O$ are in the nanocrystalline or amorphous state as-deposited at all the temperatures, as presented in Fig. 3b. In contrast to the amorphous n-type oxide semiconductor such as SnO_2, ZnSnO, and InGaZnO, the amorphous structure of p-type SnO is unfavorable for applications in p-channel TFTs because the hybridization of O 2p orbital with Sn 5s orbital results in a hole conduction pathway with a directional property. Considering that the polycrystalline ALD SnO films were achieved using $Sn(dmamp)_2/H_2O$ above 150 °C [33], the reason for the formation of the amorphous SnO films upon using $Sn(edpa)_2$ is as of yet clear; however, it could be closely related to the different ligand structures of $Sn(edpa)_2$ and $Sn(dmamp)_2$. Amorphous-like SnO film grown at 120 °C was annealed at 450 °C in N_2 ambient. Thereafter, the crystalline property was examined by XRD, as shown in Fig. 3c. The

film exhibited evident diffraction peak corresponding to polycrystalline SnO (001) and (002) planes, indicating that the polycrystalline SnO film was formed after the annealing process.

Figure 4 shows the surface topography of ~20 nm-thick SnO_2 and SnO films scanned by AFM. As shown in Figs. 4a and b, as-deposited SnO_2 films at 120 and 220 °C by $Sn(edpa)_2/O_2$-plasma process exhibited grain-like morphology with RMS roughness values of 1.2 and 1.7 nm, respectively. Meanwhile, the topography of the SnO films from the $Sn(edpa)_2/H_2O$ ALD with RMS roughness of 0.2–0.3 nm appears to be significantly smoother than those of the SnO_2 films. This is likely to be owing to the amorphous (or nanocrystalline) nature of the as-deposited SnO film (Figs. 4c–e). As depicted in Fig. 4f, after 450 °C N_2 annealing, the SnO film exhibited a crystallized structure with an enlarged grain size of 100–200 nm. After post annealing, the poly-crystallized SnO film matches reasonably with the XRD observation shown in Fig. 3c.

The optical band gap of the SnO_x films was measured using the Tauc plot ($\alpha h\nu$ vs $h\nu^{1/n}$, where α is the absorption coefficient calculated as $2\pi k/\lambda$, and n values of 1/2 were used for estimating the indirect band gap). As shown in Figs. 5a and b, optical interband absorptions were observed in the SnO_2 and SnO films. The direct band gap of the SnO_2 films was in the range of 3.6–4.0 eV, which is reasonably consistent with the values achieved with other deposition techniques such as sputtering and pulse laser deposition [39,40]. The SnO_2 films deposited at 70–220 °C exhibited a marginally stronger band-tail near the band edge as compared to that deposited at 300 °C. In contrast, the amorphous SnO films exhibited lower indirect band gap energy values (in the range of 2.9–3.0 eV). Accordingly, distinct transmittance features were observed with the SnO_2 and SnO films in visible light, as shown in Fig. 5c. The SnO_2 film grown at 120 °C was highly transparent in the range of 400–700 nm (> 85%), whereas the SnO film exhibited a lower transmittance of > 60%.

To evaluate the electrical properties of the SnO_2 and SnO films, Hall measurements were performed, as depicted in Fig. 6. The SnO_2 film exhibited a negative Hall coefficient, indicating

an n-type carrier conduction. The carrier concentration of the SnO_2 films increased dramatically (from 8.5×10^{16} to 1.2×10^{20} cm^{-3}) with an increase in the growth temperature from 120 to 300 °C. The resistivity of the SnO_2 films changed significantly (from 3×10^1 to 4×10^{-3} Ω·cm) with an increase in the growth temperature, which may be ascribed to the increased carrier concentration and crystallinity achieved at high growth temperatures. Hall mobilities of 2–26 cm^2/V·s were achieved, with the highest value of 26 cm^2/V·s at a deposition temperature of 220 °C. The Hall measurement results obtained from the 70 °C-grown SnO_2 film was not reliable owing to its high resistivity. We could not obtain reproducible results with the SnO film, probably owing to the ineffective hole transport property and high film resistivity of the SnO films.

As verified previously, the SnO_x ALD processes in this study provide a reasonable phase (composition)-controllability between SnO_2 and SnO. Therefore, a nanolaminate film composed of alternate amorphous SnO and polycrystalline SnO_2 layers was fabricated on a TiN substrate at 120 °C. 210 cycles of SnO_2 PEALD followed by 580 cycles of SnO ALD were repeated three times to produce the laminate structure shown in Fig. 7a. The thicknesses of the SnO_2 and SnO films were approximately 16 and 15 nm, respectively. In the bright field TEM image, each layer is clearly distinguished owing to the difference in the O/Sn composition ratio and the degree of diffraction contrast of the polycrystalline SnO_2 and amorphous SnO layers. The XPS depth profile shown in Fig. 7b reveals a periodic change in the Sn and O atomic percentage, indicating the successful growth of SnO_2 on SnO and vice versa. The HRTEM image of the sample recorded near the SnO_2/SnO interface (Fig. 7c) indicates the formation of an amorphous (with partial nanocrystalline) SnO film on the polycrystalline SnO_2 film. SnO_2 (101) and (110) lattice planes with a d-spacing of 0.26 and 0.33 nm, respectively, are clearly visible on the SnO_2 layer, which is reasonably consistent with the XRD results. The fast Fourier transform (FFT) patterns of the marked areas shown in Fig. 7c indicated the polycrystalline and amorphous natures of the SnO_2 and SnO films, respectively.

The surface reaction mechanisms of the SnO_2 and SnO formation by ALD were investigated by in-situ QMS at 120 °C. During the QMS analysis, the ALD processes were conducted using modified pulse conditions of 12 s ($Sn(edpa)_2$)–60 s (Ar purge)–5 s (O_2-plasma or H_2O)–60 s (Ar purge). Sufficient Ar purge time (60 s) was used to ensure that the achieved QMS signals are obtained as a result of surface reaction rather than gas phase reaction. According to the reports on the surface reaction of oxide ALDs, various types of by-product gases are likely to be obtained from both the ALD processes: namely, $edpaH^+$ (m/z = 145) from a ligand exchange reaction and CO_2^+ (m/z = 44), NO^+ (m/z = 30), and H_2O^+ (m/z = 18) from a combustion reaction. Figure 8a shows the change in the intensity of the m/z = 44 signal achieved during an ALD cycle of both the SnO_2 and SnO deposition processes. For the SnO_2 PEALD, a sharp m/z = 44 signal was observed at the O_2-plasma pulse step, whereas no signal was observed during the Sn-precursor step. This indicates the production of CO_2 gas by the combustion of edpa ligands only at the O_2-plasma pulse step. The m/z = 44 signal attained the maximum intensity in a short time of 1 s, after which it started to decrease rapidly. This implies a high combustion rate of the absorbed Sn-precursor at the O_2-plasma step. However, there is a negligible CO_2 formation during the SnO ALD process at both the Sn-precursor and H_2O pulse steps, indicating that the surface reaction during the SnO ALD does not involve a combustion reaction. The inset in Fig. 8a shows the variation of the m/z = 30 signal, verifying the formation of NO_x species because the $Sn(edpa)_2$ precursor contains N atoms in the ligand. Analogous to the CO_2 signal observed during the SnO_2 PEALD, a strong peak was observed only at the O_2-plasma pulse step, indicating the production of NO by ligand combustion. Although there was a marginal increase in the intensity of the m/z = 30 signal for the case of SnO ALD, it may be attributed to the fragmentation of the edpa ligands and not to a NO reaction by-product.

To examine the release of ligands, the signals corresponding to $edpaH^+$ (m/z = 145) and $^tBu^+$ (m/z = 57, one of the dissociative fragments of edpaH) were analyzed as shown in Fig. 8b. As depicted in the inset of Fig. 8b, the parent $edpaH^+$ signal could not be detected, probably

because of the cracking of the edpaH ligand by electron ionization. Hence, we analyzed its highest fragment peak at m/z = 57 [35]. For the SnO ALD, a signal corresponding to $^{t}Bu^{+}$ was observed at both the Sn-precursor and H_2O pulse steps, indicating the release of complete edpaH ligands as a result of a ligand exchange reaction. The release of edpaH during the SnO ALD is likely because the ALD growth of oxide films in the presence of H_2O as the reactant is generally known to involve H-transfer reaction and hydrolysis reaction at the metal-precursor and H_2O pulse steps, respectively [41,42]. It is noteworthy that the evidence for the release of edpaH was observed in the SnO_2 PEALD process notwithstanding the absence of H_2O as the reactant. This is likely to have been caused by the formation of H_2O as a by-product during the O_2-plasma pulse step, which functions as a reactant along with O_2-plasma.

Conclusion

ALD processes of SnO_2 and SnO films were successfully developed by employing $Sn(edpa)_2$ as the Sn-precursor and O_2-plasma or H_2O as the reactant. The SnO_2 and SnO films were obtained with remarkable phase controllability, which is facilitated by different surface reaction mechanisms of the $Sn(edpa)_2/O_2$-plasma and $Sn(edpa)_2/H_2O$ processes. Combustion and ligand exchange reactions occur with SnO_2 and SnO ALD, respectively. Impurity-free films were obtained even at relatively low growth temperatures of 70–180 °C. The as-deposited SnO_2 films obtained with O_2-plasma exhibited a polycrystalline structure, whereas amorphous SnO films were obtained at all the investigated temperatures. The optical band gaps of SnO_2 and SnO films were measured to be 3.6–4.0 and 2.9–3.0 eV, respectively. Sequential depositions of SnO_2 and SnO films resulted in the formation of an SnO_2/SnO multilayer heterojunction with an evident phase distinction between the SnO_2 and SnO layers. The phase controlled ALD growth of SnO_2 and SnO films in this study exhibits high potential for utilization for various applications such as TFTs, gas/photo sensors, photovoltaics, and catalysts.

Acknowledgements

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Figure captions

Fig. 1 Variations of growth rate in (a) $Sn(edpa)_2$/O_2-plasma and (b) $Sn(edpa)_2$/H_2O ALD

processes at growth temperature of 120 °C as a function of Sn-precursor and reactant pulse

lengths. (c) Changes in growth rate in $Sn(edpa)_2$/O_2-plasma and $Sn(edpa)_2$/H_2O ALD processes

at various stage temperatures of 70−300 °C. (d) Refractive index of SnO_x films deposited with

$Sn(edpa)_2$/O_2-plasma and $Sn(edpa)_2$/H_2O at 70−300 °C.

Fig. 2 (a) Sn 3d XP spectra of SnO_x films deposited by O_2-plasma or H_2O at different

temperatures. XPS depth profiles of SnO_x films grown at 120 °C with (b) $Sn(edpa)_2$/O_2-plasma

and (c) $Sn(edpa)_2$/H_2O processes.

Fig. 3 GAXRD patterns for SnO_x films grown at various temperatures using (a) $Sn(edpa)_2/O_2$-plasma and (b) $Sn(edpa)_2/H_2O$ (c) XRD pattern of SnO film after N_2-ambient annealing at 450 °C.

Fig. 4 AFM images of as-deposited SnO_2 films at (a) 120 °C and (b) 220 °C. Topography of SnO films deposited at (c) 120 °C, (d) 180 °C, and (e) 250 °C. Surface morphology of SnO film after post-deposition annealing at 450 °C in N_2 ambient.

Fig. 5 Tauc plots of (a) SnO_2 and (b) SnO films grown at different deposition temperatures. (c) Comparison of transmittances of SnO_2 and SnO films deposited at 120 °C.

Fig. 6 Carrier concentration, Hall mobility, and resistivity of SnO_2 films grown at 120–300 °C

Fig. 7 (a) Bright field TEM image of SnO_2/SnO nanolaminate grown on TiN substrate, (b) XPS depth profiles of SnO_2/SnO nanolaminate, and (c) HRTEM image of nanolaminate film near the SnO_2/SnO interface. The inset shows the FFT patterns of the marked areas.

Fig. 8 (a) Variations of CO_2^+ (m/z = 44) signal intensity during an ALD cycle of SnO_2 and SnO processes. The inset shows the variation in the NO^+ (m/z = 30) signal during the process. (b) Variation for $^tBu^+$ (m/z = 57) intensity during an ALD cycle of SnO_2 and SnO processes. The inset shows the variation of the complete $edpaH^+$ (m/z = 145) ligand signal.
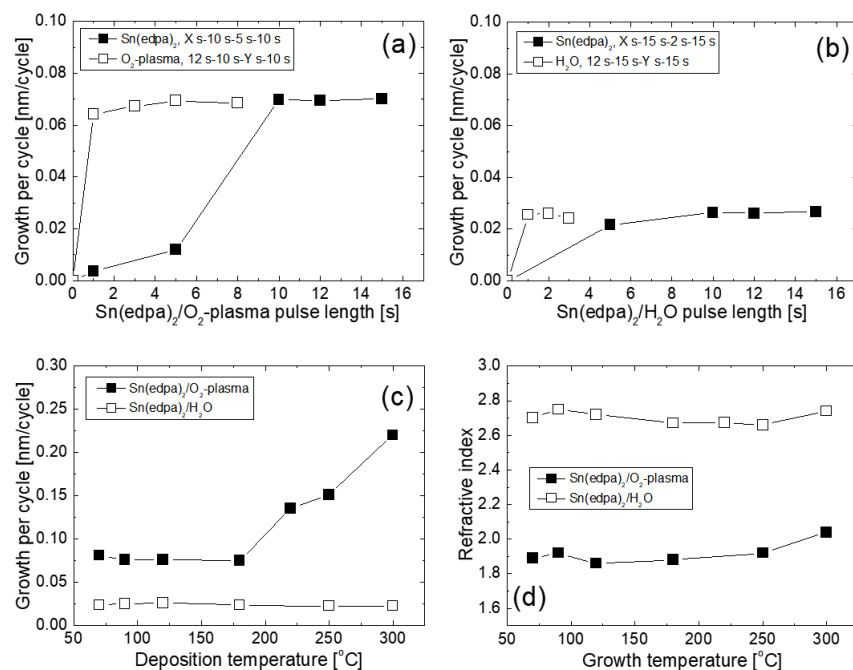
Fig. 1

Fig. 2

Fig. 3

Fig. 4

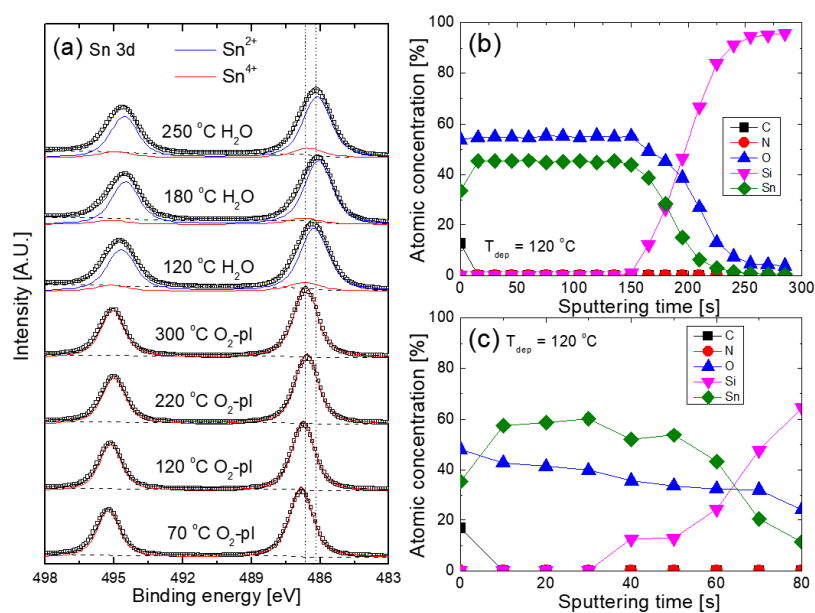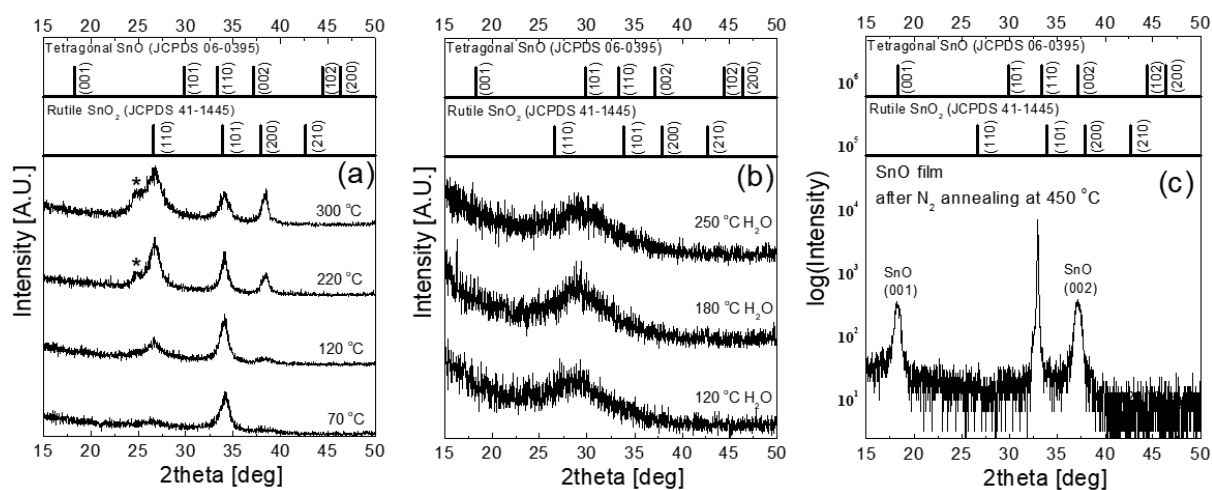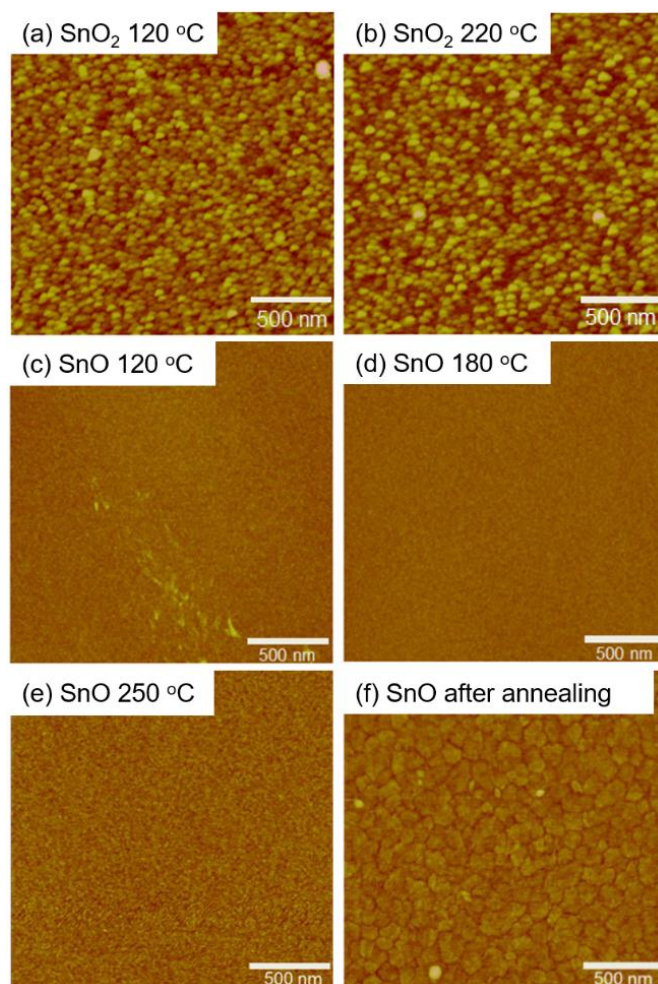(a) SnO₂ 120 °C (b) SnO₂ 220 °C
(c) SnO 120 °C (d) SnO 180 °C
(e) SnO 250 °C (f) SnO after annealing

Fig. 5

Fig. 6

Fig. 7

Fig. 8