



Effects of atmosphere composition during direct ultraviolet-light patterning of solution-deposited In₂O₃ thin film transistors

Trey B. Daunis⁺, Weijie Xu⁺, Sampreetha Thampy, Marisol Valdez, Julia W.P. Hsu^{*}

Department of Materials Science and Engineering, University of Texas at Dallas, 800 W Campbell Rd, Richardson, TX 75080, USA

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ABSTRACT

Sol-gel synthesis is widely used to fabricate metal oxide thin films by solution, but it requires high-temperature thermal annealing to fully convert precursors to metal oxides. Exposure to Ultraviolet (UV) light before thermal annealing of precursor films has been shown to reduce the conversion temperature, with the added benefits of film patterning when done through a shadow mask and improved device performance. However, the mechanism by which UV exposure under different atmospheric compositions affects the properties of metal oxide films after thermal annealing has not been investigated. Here, we control the atmospheric composition during UV-patterning—prior to high-temperature thermal annealing—of In₂O₃ sol-gel films which serve as the semiconductor in thin-film transistors. Despite all films being annealed at 250°C in air after UV patterning, films exposed to UV under oxygen-containing atmospheres have higher metal-oxygen-metal bonding and exhibit higher transistor mobility compared to the films exposed to UV under N₂ atmosphere. The origin of the effect of atmospheric composition on mobility is studied through X-ray photoelectron spectroscopy (XPS) and Fourier-transform infrared spectroscopy and is revealed to be the result of the reformation of the nitrate species in the films under more oxidizing atmospheres during UV exposure. These nitrates can be completely removed by thermal annealing, facilitating more complete metal-oxygen-metal bond formation, which is reflected in higher O_{1s} XPS signal and transistor mobility. In contrast, films processed under N₂ atmosphere during UV exposure contain nitrite species that cannot be removed by thermal annealing, resulting in less metal-oxygen-metal bond formation and lower mobility.

1. Introduction

Metal oxides are ideal materials for many thin-film electronic applications due to their greater long-term stability compared to organics and their wide variety of electronic properties including dielectric, semiconducting, ferroelectric, and transparent conducting behaviors [1, 2]. Sol-gel chemistry is widely used for the fabrication of metal oxide films by solution [3]. A high-temperature, typically > 400°C, thermal annealing step is needed to convert the sol-gel precursors to metal oxides. Recent interest in using metal oxide films for flexible electronics drives the need to lower the processing temperature to be compatible with plastic substrates [4,5]. It was shown that exposing sol-gel precursor films to ultraviolet (UV) light prior to thermal annealing is effective in lowering the conversion temperature while producing good device performance [6–9]. When performed through a shadow mask, patterned films are produced due to selective conversion of the UV

exposed areas; subsequent rinsing in a developing solution removes the precursor in the unexposed regions [10–12]. Additionally, it has been reported that UV exposure prior to thermal annealing improves the properties of the annealed oxide film compared to thermal annealing only without UV treatment [8,13].

The effect of UV irradiation on the conversion of metal-nitrate precursors to metal oxides is currently understood to be due to the generation of oxygen-radical species through the photolytic decomposition of nitrate ions [9,14,15]. This decomposition pathway involves multiple reactive oxygen species and results in the formation of metal-oxygen-metal (M-O-M) bonds. UV exposure alone is not sufficient to fully convert sol-gel precursor films to metal oxides and additional thermal annealing is needed [10]. Furthermore, while some studies perform the UV exposure in an N₂ atmosphere [7,16,17] or prevent oxygen and UV-generated ozone from contacting the sample by using a hard contact quartz photomask during UV patterning [12], other studies

^{*} Corresponding author.

E-mail address: jwhsu@utdallas.edu (J.W.P. Hsu).

⁺ These authors contributed equally.

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perform UV exposure in air in the presence of both atmospheric oxygen and UV-generated ozone [18–20]. While successful patterning was reported in these publications, *how UV exposure under different atmospheres affects the properties of fully converted metal oxide films after thermal annealing, and the mechanism by which this occurs, has not been investigated.*

Here, we control the atmospheric composition during UV patterning of solution-deposited In_2O_3 sol-gel films prior to 250°C thermal annealing. The atmospheric effects on the chemical properties of the final oxide films and thin-film transistor (TFT) devices are examined and elucidated. The chemical properties of the films after UV exposure and after thermal annealing are evaluated through X-ray photoelectron spectroscopy (XPS) and Fourier-transform infrared (FTIR) spectroscopy. Since many oxide semiconductors and dielectrics have been processed using similar methods, our study of In_2O_3 can be applied to other binary oxides made from nitrate precursors [21,22].

2. Experimental details

2.1. In_2O_3 Precursor Film Deposition

The In_2O_3 precursor solution was prepared by dissolving 0.1M $\text{In}(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$ in 2-methoxyethanol, followed by the addition of 0.1M NH_4OH and 0.1M acetylacetone. The solution was stirred at room temperature for 48 h prior to film deposition. The resulting solution strongly absorbs UV light with a wavelength < 320 nm [10]. Gold-coated p^{++} silicon substrates for XPS, undoped (intrinsic) silicon substrates for FTIR, and p^{++} silicon wafers with 177 nm thermally grown SiO_2 (measured by ellipsometry, J.A. Woollam M2000DI) for TFTs were rinsed in acetone, isopropyl alcohol, and deionized water (DI) water followed by UV-ozone treatment (Bioforce Nanosciences Procleaner Plus) for 20 min prior to In_2O_3 deposition. The In_2O_3 precursor solution was spin coated onto the prepared substrates at 3,000 rpm for 30 s, and the samples were immediately dried on a hotplate at 80°C for 3 min. The thickness of the precursor film is ~ 28 nm [10].

2.2. Patterning Treatment and Annealing

Prior to 250°C thermal annealing, dried precursor films were treated by one of four methods in the UV-ozone apparatus (Samco model UV-1): ozone (O_3) only, UV in a nitrogen atmosphere (UV- N_2), and UV with ozone generated both *in-situ* from the air by the UV radiation (UV-Air) and *ex-situ* in an ozone generator (UV- O_3). Samples for TFTs first had a 0.005" thick invar shadow mask placed on top which was held in place by a magnet on the bottom of the sample. Samples for XPS and FTIR analysis were treated without a mask but were placed on top of the same magnets to ensure the same distance between the sample and UV light source. For O_3 -only and UV- O_3 , oxygen was flowed through the external ozone generator at 0.5 L per min (lpm) and then into the sample chamber without (O_3 -only) or with (UV- O_3) the low-pressure mercury UV lamp (254 nm and 185 nm radiation) turned on. For UV- N_2 , the chamber was purged with N_2 at 3 lpm for 5 minutes prior to exposure to UV, and the chamber was continuously purged with N_2 during UV exposure. For UV-Air, samples were processed without purging by closing the chamber and turning on the UV lamp. Samples were exposed to UV for 10 min. Patterning experiments were performed at 90°C to avoid an increase in temperature from the UV light during exposure. Following the treatment, the shadow masks were removed and the samples were dipped into a developing solution (15 mL DI water, 5 mL methanol, and 1 mL acetic acid) for 5 s to remove the unexposed precursor film followed by a thorough rinse in DI water. All patterned films were then annealed on a hotplate at 250°C in air for 20 min. The film thickness differs by less than 10% for the three atmospheric compositions: ~ 13 nm after UV exposure and ~ 7 nm after thermal annealing, which is not affected by the developing solution [10]. The complete process for deposition of In_2O_3 films is shown schematically in Fig. 1.

2.3. X-ray Photoelectron Spectroscopy

XPS was performed on a Ulvac-PHI VersaProbe2 with a monochromated Al K α source (1486.8 eV) at an angle of 45° to the sample surface at 50 W and 15 kV with a 200 μm beam size. Scanning was performed with an energy step of 0.2 eV at 20 ms per step and a pass energy of 23.5 eV. All spectra are averaged over 20 scans. XPS data were

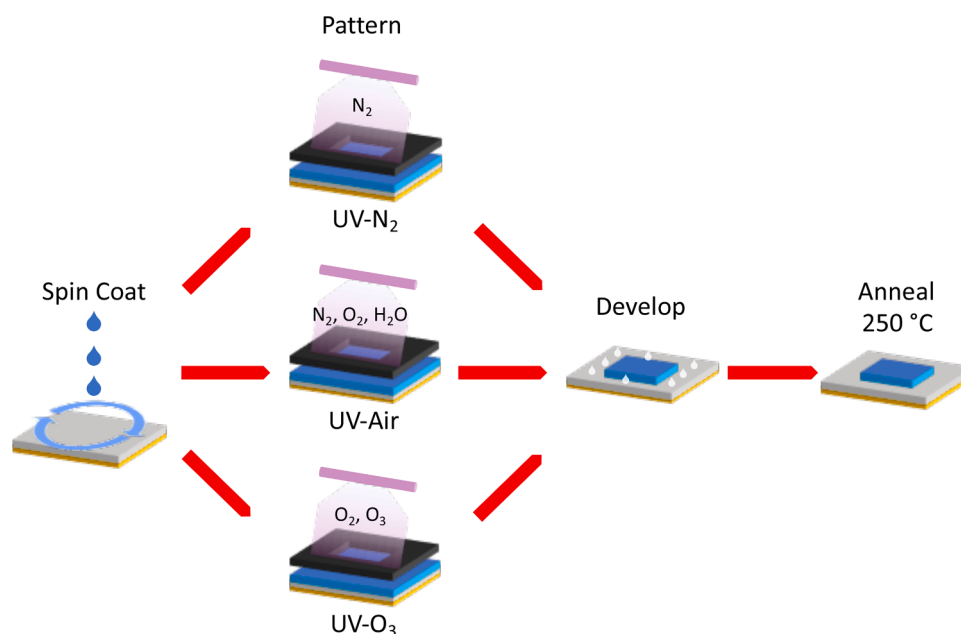


Fig. 1. Schematics of In_2O_3 film processing. From left to right, In_2O_3 sol-gel precursor is spin coated on a Si/ SiO_2 substrate and the dried film is exposed through a shadow mask to a UV lamp in nitrogen (UV- N_2 , top), air (UV-Air, middle), or ozone (UV- O_3 , bottom) atmosphere. The samples are rinsed in a developing solution to remove the unexposed areas and are annealed on a hotplate at 250°C in air for 20 min.

analyzed using commercial software (MultiPak, Ulvac-PHI).

2.4. Fourier-Transform Infrared Spectroscopy

FTIR measurements were performed in a Nicolet iS50 spectrometer with a mercury cadmium telluride (MCT-A) detector under N₂ purge. All spectra were collected with a resolution of 4 cm⁻¹ in the range of 650–4000 cm⁻¹. The sample spectra were referenced to the spectra of the bare intrinsic silicon substrates, and residual water vapor absorption signals were removed by subtraction.

2.5. Spectroscopy Ellipsometry

Spectroscopic ellipsometry measurements (M-2000DI, J. A. Woolam) at 55°, 65°, and 75° incident angles from 300 to 1690 nm in wavelength were done to determine the thickness and optical constants of films. The fitting was performed using a Cauchy model between 600 and 1690 nm.

2.6. Atomic Force Microscopy

Film roughness was measured using an atomic force microscope (Asylum MFP-3D). 5 μm x 5 μm Atomic Force Microscope (AFM) images were taken at three different locations.

2.7. Transistor Fabrication and Measurements

To finish the transistors, 100 nm Al source and drain contacts were deposited by thermal evaporation through a shadow mask to define a channel with a width of 1,000 μm and length of 100 μm. Metal-insulator-metal capacitors were defined by 400 μm x 400 μm Al top contacts in regions where the In₂O₃ was removed by the patterning process, and the capacitance of the gate dielectric, used in calculating the channel mobility, was measured using an Agilent 4284A Precision LCR Meter at 10 kHz with 0 V DC bias and 50 mV AC amplitude. Transfer output curves were measured in a Keithley 4200-SCS Semiconductor Characterization System with drain voltage at 35 V for transfer curve measurements to ensure saturation operation of the transistors.

3. Results and discussion

When performing patterning using UV in air [10,19,20], partial conversion of metal oxide films can be due to exposure to the high energy of UV light, the reactive oxygen atmosphere, or both. To separate the contributions from these effects, we first exposed In₂O₃ precursor films to ozone only (O₃-only) or UV only with no ozone or oxygen (UV-N₂) to determine whether reactive oxygen species or UV light is the necessary component for film patterning. Films exposed to O₃-only showed no chemical resistance to the developing solution even after one hour of exposure. The entire film, in both exposed and unexposed regions, was removed by the developing solution. However, films exposed to UV light only (UV-N₂) for just 10 min showed excellent contrast after developing, with the exposed regions remaining on the substrate. Thus, *UV is the necessary component responsible for the initiation of metal oxide conversion*. Exposure to mercury vapor lamp emission through glass optics that blocks the shorter wavelength UV light was also found to produce no patterns, suggesting that it is the strong emissions at 185 nm and/or 254 nm which are responsible for conversion. Our result confirms previous reports that suggest the decomposition of nitrates induced by UV photons [9,23]. While we show that ozone alone is not enough to initiate conversion to metal oxide, we are curious whether the presence of ozone in combination with UV during patterning has a positive or negative effect: on one hand, oxygen and ozone can absorb UV light and reduce UV intensity delivered to the sample, but on the other hand, reactive oxygen species were proposed to facilitate M-O-M bond formation and film densification [24,25]. To examine these effects, we prepared films under three different atmospheric conditions: UV-N₂,

UV-Air, and UV-O₃, as shown in the second step in Fig. 1. The four-step process depicted in Fig. 1 consists of depositing the sol-gel precursor film, patterning with UV exposure under various atmospheric compositions, developing the pattern, and finally annealing the oxide film thermally.

3.1. Transistor Performance

Transistors were fabricated using a p⁺⁺ silicon substrate as the back gate with a 177 nm thick thermal SiO₂ layer as the gate dielectric. Fig. 2a shows the transfer curves measured on devices with 250°C-annealed In₂O₃ semiconductor layer but patterned under each of the three UV exposure atmospheres. Fig. 2b shows the drain current vs. drain voltage output characteristics of each device demonstrating saturation regime operation for the measurement conditions used in Fig. 2a. The field effect mobility (μ_{FE}) for each device was extracted using the saturated mobility equation:

$$\mu = \left(\frac{d\sqrt{I_D}}{dV_G} \right)^2 \frac{L}{WC}$$

where I_D is the drain current, V_g is the gate voltage, L is the channel length, W is the channel width, and C is the areal gate capacitance. The values for $\frac{d\sqrt{I_D}}{dV_G}$ were extracted from linear fits (thin solid lines) to the I_D^{1/2} vs. V_G data (dashed lines) plotted on the right y-axis in Fig. 2a. While each type of device has a similar threshold voltage of ~ 4 V, the UV-N₂ device (red) has the lowest mobility (1.9 ± 0.5 cm² V⁻¹s⁻¹), followed by UV-Air (light blue, 3.1 ± 0.7 cm² V⁻¹s⁻¹), and UV-O₃ (dark blue, 4.4 ± 0.7 cm² V⁻¹s⁻¹) which has the highest mobility within one batch. Two more batches were made, and the mobility of at least 7 devices was examined to further confirm the statistical difference between the 3 conditions (Fig. 2c). As all devices were annealed at 250°C after the patterning step, the distinct mobility difference shows that *the atmospheric composition during the UV patterning step is critical in determining the semiconductor films' eventual electrical properties*, which cannot be erased even after thermal annealing. This is unexpected because the thermal annealing step involves both a significantly higher temperature (250°C vs. 90°C) and longer duration (20 vs. 10 min) than the patterning step, and it suggests that the chemical or morphological changes induced by the atmospheric composition during the initial patterning step either persist after thermal annealing or affect the thermal annealing process. We applied AFM to examine whether there are any morphological differences. The roughness of UV-N₂, UV-air, and UV-O₃ is 0.69 ± 0.02, 0.74 ± 0.01, and 0.70 ± 0.04 nm, respectively. Their similarity suggests that morphological differences do not play a critical role here.

3.2. Metal-oxygen Bond Formation Probed by XPS

To examine the film chemistry associated with the varying atmospheric conditions during UV exposure and the potentially lasting effects, we performed XPS on each type of film after UV exposure and after the 250°C annealing step. In previously reported studies, oxide semiconductor films with a larger percentage of O_I peak at ~529.5 eV (attributed to M-O-M bonding) in the O 1s XPS spectra show higher field effect mobilities [18,19]. Fig. 3 compares the O 1s region of the XPS spectra for the three UV exposure conditions. Each O 1s peak is deconvoluted into three Gaussian peaks, O_I at ~529.5 eV (blue curves), O_{II} at ~531.5 eV (green curves), and O_{III} at ~532.5 eV (orange curves). The shape of these peaks (full-width half-max and percent Gaussian characteristic) were fixed between the fitting for all samples, with the position and height allowed to vary.

Previously we showed that UV exposure increases the O_I contribution in the O 1s peak, consistent with M-O-M formation in the precursor films that make them resistant to developing solution [10]. Here we further show that the O_I contribution depends on the atmospheric

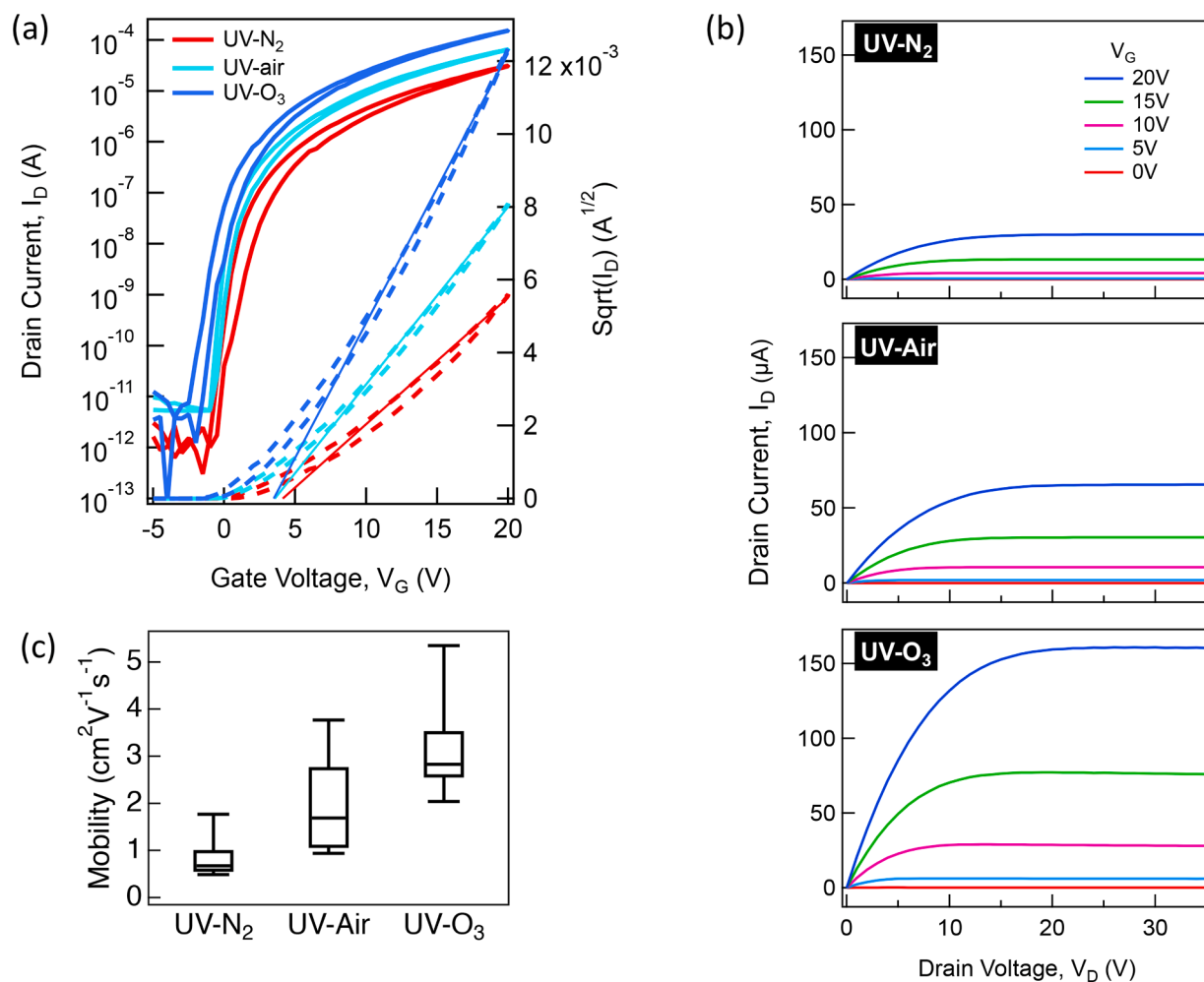


Fig. 2. TFT performance for In_2O_3 transistors on Si/SiO_2 substrates. (a) Transfer curves for In_2O_3 patterned using UV- N_2 (red), UV-Air (light blue), and UV- O_3 (dark blue). A linear fit (thin solid lines) of the forward scan of $I_D^{1/2}$ (dashed lines, right axis) in the linear region from 10 V to 20 V is used for the calculation of mobility. V_D is 35 V. (b) Output curves for In_2O_3 patterned using UV- N_2 (top), UV-Air (middle), and UV- O_3 (bottom) showing saturation operation of the transistors at the voltages used in the transfer curves. (c) Statistical analysis of TFT mobility on at least 7 devices.

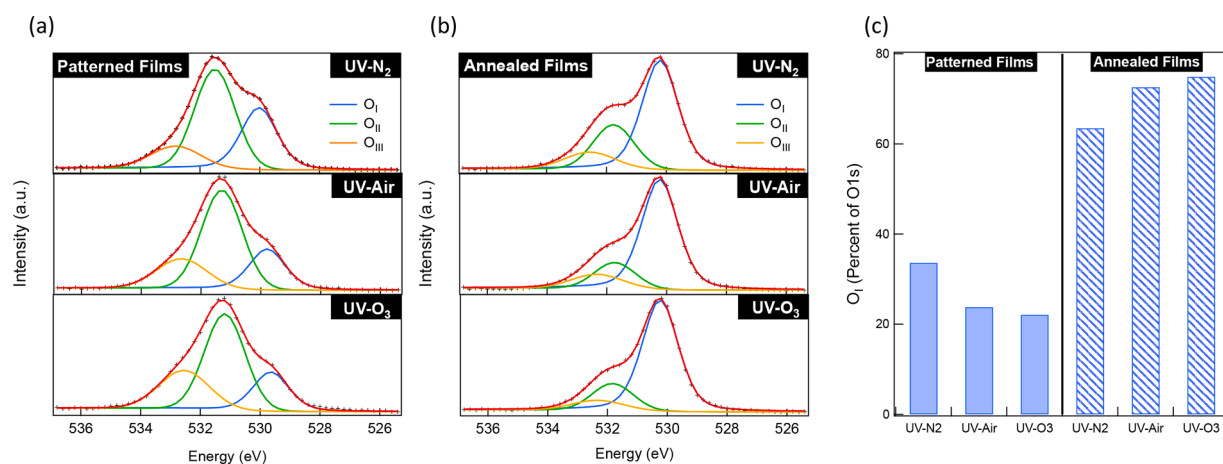


Fig. 3. O 1s XPS spectra. (a) Films patterned using UV- N_2 (top), UV-Air (middle), and UV- O_3 (bottom). (b) Films from (a) after annealing at 250°C in air. O 1s peaks (measured data shown with black crosses, fitting with red curves) are deconvoluted into three peaks: O_I (blue curves) at ~ 529.5 eV, O_{II} (green curves) at ~ 531.5 eV, and O_{III} (orange curves) at ~ 532.5 eV. (c) Area under the O_I peak as a percent of total O 1s area for each plot in (a) and (b). Solid bars represent patterned films and hashed bars represent thermally annealed films.

composition during UV exposure. Fig. 3a shows that after UV exposure (termed “patterned films”), the O_1 peak contributes to a significantly larger percentage of the O 1s signal for the UV- N_2 sample compared to the two samples exposed to oxygen-containing atmospheres, and has the smallest contribution for the UV- O_3 sample. After 250°C thermal annealing in air (termed “annealed films”), the O_1 peak contribution increases drastically and becomes the dominant component in the O 1s region for all samples (Fig. 3b), confirming that high-temperature thermal annealing is needed to fully convert the samples to metal oxides. However, the trend of relative O_1 peak contribution for the annealed films is opposite to that for the patterned films, with the UV- O_3 sample exhibiting the largest percentage of the O_1 peak. Fig. 3c shows the area under the O_1 peak as a percentage of the total O 1s peaks for the UV-exposed films made under each condition (solid bars) and for the annealed films (hashed bars). In a simplistic mechanism in which the UV patterning process initiates M-O-M bonding and the thermal annealing process further completes the bond formation, the expected outcome is for both the patterned and annealed films to exhibit the same trend in the O_1 fraction, i.e., UV- $N_2 >$ UV-Air $>$ UV- O_3 , or for the O_1 peak areas to become equal for all methods after thermal annealing if thermal annealing erased the previous processing history. However, the experimental results show a reverse trend, i.e., O_1 fraction increases as UV- $N_2 <$ UV-Air $<$ UV- O_3 after thermal annealing. This surprising result signals that additional and lasting changes are produced by the atmospheric composition during the UV patterning, which affects the final thermal-annealing outcome. We note that the extent of M-O-M bonding (percent O_1 in O 1s) of the annealed films is consistent with the performance of the transistors: the UV- O_3 device has the highest mobility and the largest extent of M-O-M bonding while the UV- N_2 device has the lowest mobility and the smallest extent of M-O-M bonding.

3.3. Evolution of Nitrogen Species

As decomposition of nitrates is thought to be the first step in conversion from sol-gel precursors containing metal nitrates to metal oxide films during UV exposure [9], we compare the N 1s region of the XPS spectra and the NO_x region from FTIR for each type of film after UV exposure (patterned films) and after thermal annealing in air (annealed films). The N 1s region for all patterned films (Fig. 4a, solid lines) shows two peaks centered at around 407 eV and 404 eV corresponding to nitrate (NO_3^-) and nitrite (NO_2^-) ions, respectively [21]. This indicates that the NO_3^- precursor is not fully decomposed during UV exposure regardless of the atmospheric composition. However, the UV- N_2 patterned film (top, red solid) shows a NO_2^- peak with intensity slightly larger than the NO_3^- peaks, while the UV-Air (middle, light blue solid) and UV- O_3 (bottom, dark blue solid) patterned films show a large NO_3^- peak and a negligible NO_2^- peak. While NO_3^- is present in the precursor solution, NO_2^- is not, and thus must be generated during the UV exposure. After 250°C annealing (dashed lines), no NO_3^- signal is observed in any of the films, but the NO_2^- signal in UV- N_2 film remains.

To further corroborate the XPS results, we present the FTIR spectra of UV- N_2 (top, red), UV-Air (middle, light blue), and UV- O_3 (bottom, dark blue) in Fig. 4b. The UV- N_2 patterned film (red solid line) shows a broad peak from between $\sim 1300\text{ cm}^{-1}$ and $\sim 1600\text{ cm}^{-1}$, indicating the presence of NO_3^- / NO_2^- species in the sample and consistent with the XPS results. In contrast, UV-Air, and UV- O_3 patterned films (solid lines) show narrower peaks, from $\sim 1300\text{ cm}^{-1}$ to $\sim 1500\text{ cm}^{-1}$. After annealing (dashed lines), there are no peaks in the $1300\text{--}1600\text{ cm}^{-1}$ region in UV-Air and UV- O_3 films, but peaks are still present in the UV- N_2 film. From the XPS results, we know that NO_3^- species are completely removed by thermal annealing in the UV-Air and UV- O_3 films; therefore, the difference spectra between the annealed and patterned films made under UV-Air and UV- O_3 conditions (Fig. 4c light blue and dark blue curves) reflect the characteristic vibrational frequencies associated with

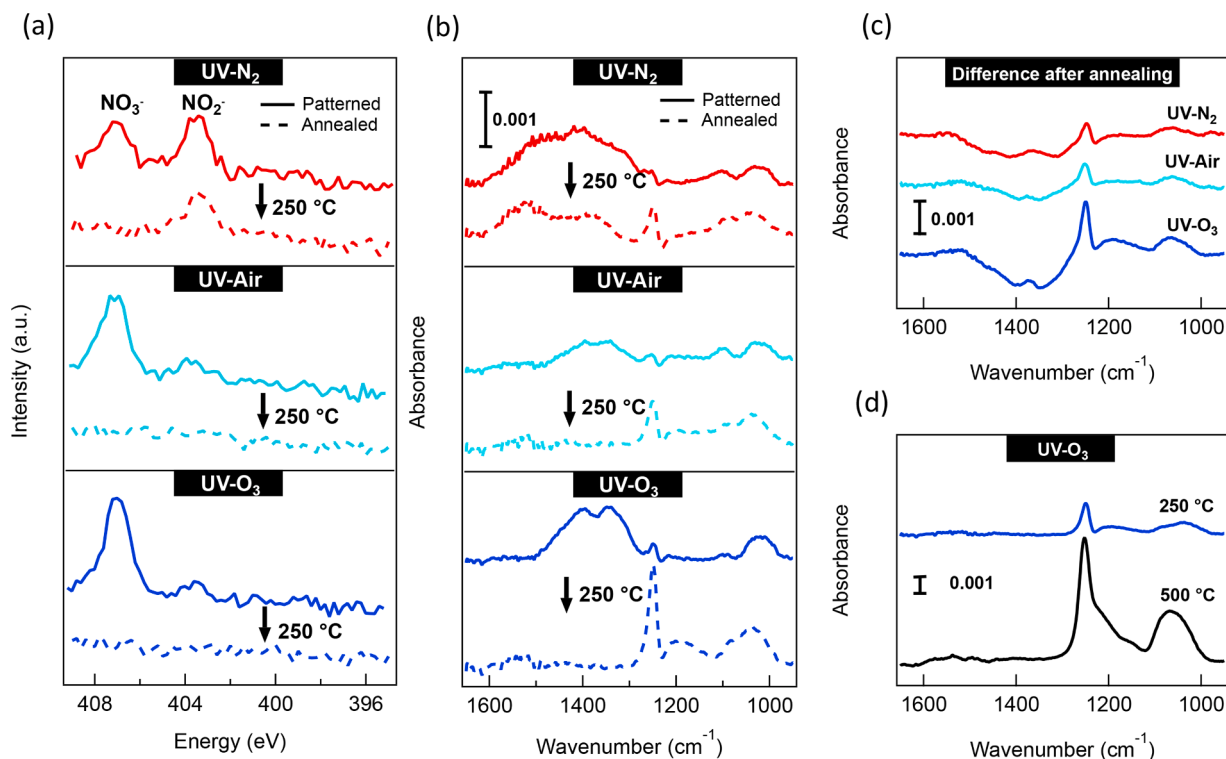


Fig. 4. (a) N 1s XPS and (b) FTIR in the NO_x absorption region for the In_2O_3 films. Spectra from top to bottom are for UV- N_2 patterned films (solid red lines) and annealed films (250°C, dashed red lines), UV-Air patterned (solid light blue lines) and annealed films (dashed light blue lines), and UV- O_3 patterned (solid dark blue lines) and annealed films (dashed dark blue lines). (c) The difference FTIR spectra between patterned and annealed films from (b). (d) FTIR spectra for a UV- O_3 film annealed at 250°C (blue) and 500°C (black), showing growth in the peaks centered at 1250 cm^{-1} and 1030 cm^{-1} .

NO_3^- species in these films. Note that the loss of FTIR signals in the annealed UV- N_2 film (Fig. 4c red curve) is similar to the other two curves, indicating that NO_3^- species in this film are also removed by annealing. The remaining FTIR signals in the annealed UV- N_2 film (Fig. 4b dashed red curve) must arise from the NO_2^- species, consistent with the XPS result (Fig. 4a, dashed red line). Our finding that NO_2^- species are not removed by thermal annealing is consistent with previous reports that NO_2^- species are more thermally stable compared to NO_3^- species [15,26].

Additionally, FTIR spectra of the patterned and especially annealed films show two peaks: at 1250 and 1030 cm^{-1} . These peaks grow after annealing the In_2O_3 films to 250°C (Fig. 4c). Further growth is observed upon annealing the UV- O_3 film to 500°C while all other absorption peaks are gone (Fig. 4d), which indicates that they are not from organic species. The intensity of these peaks correlates with the intensity of the O_1 peak in the O 1s XPS, suggesting that they arise from In-O vibrational modes in the oxide film. For silica glass made from sol-gel, the IR absorption peaks at 1220 and 1080 cm^{-1} were assigned to the longitudinal optical (LO) and transverse optical (TO) modes of Si-O-Si asymmetric stretching [27]. Therefore, we postulate that the 1250 and 1030 cm^{-1} peaks are due to the LO and TO modes of similar vibrations in the In_2O_3 film.

3.4. Film Chemistry Due to Atmospheric Effect During UV Exposure on M-O-M Bond Formation Upon Thermal Annealing

Based on the XPS and FTIR results, we can now explain the observed differences in the M-O-M bond formation in the patterned and annealed films, as summarized by the reaction schematics in Fig. 5.

From previous studies on nitrate photodecomposition mechanisms, it is well known that NO_3^- ions are excited by UV irradiation to ONOO^- ions which then decompose under continued UV irradiation into NO_2^- and an oxygen free radical ($\text{O}^\bullet$) (Fig. 5, step ii-a/b) [25,28–30]. The released oxygen then participates in M-O-M bond formation. Because the inert atmosphere does not absorb UV radiation while oxygen and ozone atmospheres do, the UV- N_2 film is exposed to a higher intensity of UV radiation than the UV-Air and UV- O_3 films. Therefore, the amount of NO_3^- that is photo-decomposed under the UV-Air and UV- O_3 processes is lower compared to that under the UV- N_2 atmosphere. This leads to the observation that in the patterned films, M-O-M bond formation, as indicated by the O 1s O_1 peak, decreases in the order of UV- $\text{N}_2 > \text{UV-Air} > \text{UV-}\text{O}_3$ (Fig. 3c, solid bars). Under an inert atmosphere, NO_2^- remains in the sample as evidenced in the N 1s XPS spectrum of the UV- N_2 film (Fig. 4a, red solid line). This is schematically shown in Fig. 5, step iii-a.

In contrast, in the presence of a strongly oxidizing atmosphere, the generated NO_2^- is readily oxidized back into NO_3^- (Fig. 5, step iii-b), explaining the minimal presence of NO_2^- signal and stronger NO_3^- signals in the N 1s XPS spectra of patterned films made under oxygen-containing atmospheres (Fig. 4a, solid light and dark blue lines).

Under 250°C annealing, not only does the NO_3^- species undergo thermal decomposition releasing NO_x gases and leaving behind oxygen in the lattice (Fig. 5, step iv-a/b), it also acts as an oxidizer in the solution combustion process to provide energy in the form of additional heat which improves M-O-M bond formation.[31] The trend of NO_3^- signals observed in Fig. 4a correlates well with the observed O_1 in O 1s XPS after annealing (Figure 3c, hatched bars). Thus, the more NO_3^- in the film after UV exposure, the more oxygen and heat is available upon its decomposition for bond formation. With a stronger bond strength [32] and greater thermal stability[26] than NO_3^- , NO_2^- remains in the final annealed UV- N_2 film (Fig. 4a, red dashed line) as illustrated in Fig. 5, step iv-a. As a result, the UV- O_3 annealed film has the highest M-O-M bonds while the low amount of NO_3^- coupled with the presence of thermally stable NO_2^- explains the low M-O-M bond formation in the annealed UV- N_2 film. Finally, the trend in the extent of M-O-M bonding of the annealed films is responsible for the trend in the mobility of the transistors, with more M-O-M bonding resulting in higher mobility.

4. Conclusions

The combined device performance and spectroscopic materials studies allow us to assess the effects of atmospheric composition during the UV exposure prior to high-temperature thermal annealing on the conversion sol-gel precursor films. Even though the final metal oxide conversion is performed by thermal annealing at a high temperature for a prolonged time, the atmospheric composition during the preceding UV-patterning step strongly affects the performance of In_2O_3 semiconductor films used as the channel in thin-film transistors. An atmosphere containing more reactive oxygen species produces a greater extent of M-O-M bonding in the oxide film after thermal annealing, and thus higher mobility, despite resulting in less UV radiation reaching the sample and less M-O-M bonding formed during UV exposure. This is because the oxidizing atmosphere reverts the photo-decomposed nitrites to nitrates. These nitrates are the source for M-O-M bond formation during subsequent thermal annealing and can be completely decomposed at a relatively lower temperature than nitrites. Thus, performing UV-patterning of sol-gel oxide films under excess oxygen and ozone is beneficial to device performance, and is preferred over performing this step in an inert atmosphere or to using a hard mask to isolate the sample

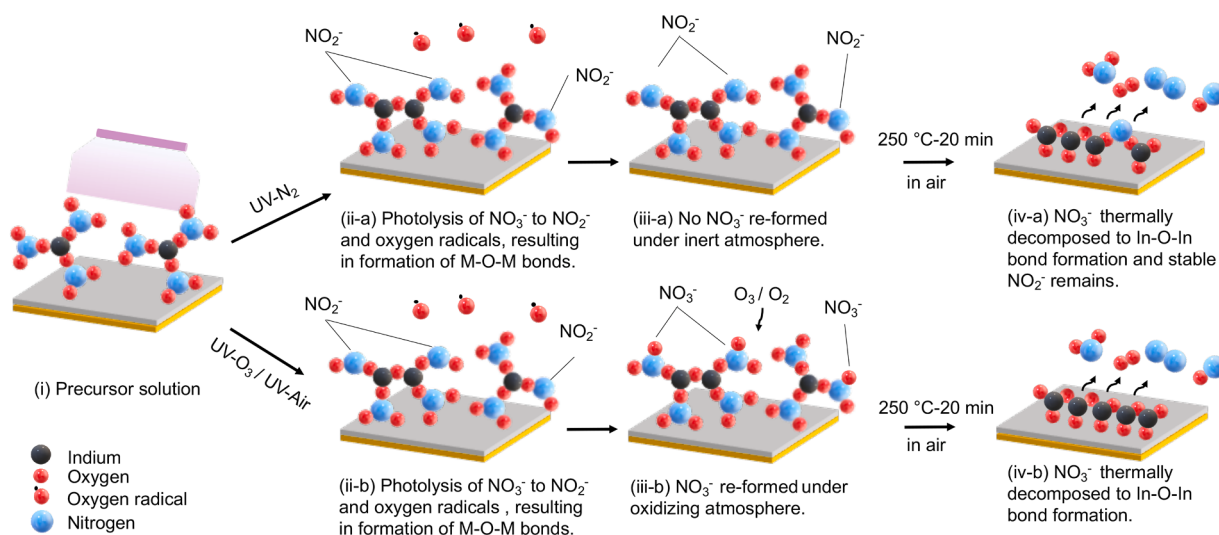


Fig. 5. Reaction schematics depicting the effects of UV exposure atmospheres on the films' chemical properties.

from ozone.

CRediT authorship contribution statement

Trey B. Daunis: Conceptualization, Methodology, Investigation, Validation, Data curation, Formal analysis, Writing – original draft. **Weijie Xu:** Conceptualization, Methodology, Investigation, Validation, Data curation, Formal analysis, Writing – original draft. **Sampreetha Thampy:** Formal analysis, Writing – review & editing. **Marisol Valdez:** Investigation, Data curation. **Julia W.P. Hsu:** Supervision, Methodology, Resources, Writing – review & editing.

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.

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