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X-ray photoelectron spectroscopy study on the chemistry involved in tin oxide film growth during chemical vapor deposition processes

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The chemistry of atmospheric pressure chemical vapor deposition (APCVD) processes is believed to be complex, and detailed reports on reaction mechanisms are scarce. Here, the authors investigated the reaction mechanism of monobutyl tinchloride (MBTC) and water during SnO2 thin film growth using x-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM). XPS results indicate an acid–base hydrolysis reaction mechanism, which is tested with multilayer experiments, demonstrating self-terminating growth. In-house developed TEM wafers are used to visualize nucleation during these multilayer experiments, and results are compared with TEM results of APCVD samples. Results show almost identical nucleation behavior implying that their growth mechanism is identical. Our experiments suggest that in APCVD, when using MBTC and water, SnO2 film growth occurs via a heterolytic bond splitting of the Sn-Cl bonds without the need to invoke gas-phase radical or coordination chemistry of the MBTC precursor. © 2013 American Vacuum Society. [http://dx.doi.org/10.1116/1.4756898]

I. INTRODUCTION

Thin films of transparent conductive oxide (TCO) like F-doped SnO2 can be deposited in a quick and economical efficient way using atmospheric pressure chemical vapor deposition (APCVD). Therefore, APCVD can be an interesting candidate to lower production costs of for example thin film solar cells or organic light-emitting diodes.1–3 APCVD positions are used at industrial scale employing moving-belt reactors to deposit large areas of glass with a SnO2 thin film for energy-conserving low-E glass and antistatic films.4 To optimize this deposition process to make APCVD suitable for high-tech applications, a detailed reaction mechanism toward film growth is needed in order to tune the intrinsic parameters of the deposition process. Literature on the growth mechanism of APCVD with RnSnCl4-x compounds is scarce and inconclusive. CVD mechanisms toward SnO2 film growth that are proposed in literature can be derived into three groups: gas-phase-driven mechanisms, surface-driven mechanisms, or a combination of both. In the first group, Gordon and co-workers published radical-driven mechanisms involving tetramethyl tin [TMT, (CH3)4Sn] or dimethyl tinchloride [DMTC, (CH3)2SnCl2] with oxygen.5,6 Based on kinetic data from both literature and their own experiments, they postulated a radical-driven gas-phase mechanism with RnSnOx species as a key intermediates that have to form in the gas phase before deposition could take place with SnO2 as result. Many years later, van Mol et al. claimed to have seen evidence for these intermediates by in situ Fourier-transformed infrared spectroscopy.7 The second group is represented by the surface reaction-driven mechanisms of tin tetrachloride [TTC, SnCl4] with oxygen or water, described by Ghoshagore.8 These Eley-Rideal-type of mechanisms are based on kinetic data and describes the deposition mechanism in two steps: first tin tetrachloride adsorbs at the surface of the substrate followed by a reaction with oxygen or water coming from the gas-phase. Although reactions of tin tetrachloride with water and oxygen are relatively fast, Eley-Rideal mechanisms are not very likely since the loss of entropy and the minimal chance that molecules collide in the exact configuration needed for a reaction will give an extremely low pre-exponential factor, and so reaction rate.9 The last great is represented by Chae et al.10,11 who interpreted their results also in terms of an Eley-Rideal-type of mechanism during his study on monobutyl tin chloride (MBTC, n-C4H9SnCl3) with oxygen. However, for the deposition of MBTC with oxygen and water, the authors proposed that first a gas-phase complex of MBTC with water must be formed before the complex can adsorb at the surface and react with oxygen in an Eley-Rideal-type of reaction. Because of these different types of mechanisms described in literature, we decided to start our own investigation of the mechanism of MBTC with water.

Supported by the publications of Basset et al. (Ref. 12 and references therein) and our experience with reactive halogen-containing organometal compounds, we believe that an acid–base hydrolysis mechanism involving the cleavage of the
Sn-Cl bonds at the film surface may play an important role. In order to investigate the importance of this surface chemistry in CVD processes of R₃SnCl₄₋ₓ species with water, we built a low-pressure reaction set-up (Fig. 1). The low pressure (10⁻⁸–10⁻⁶ mbar) is necessary to slow down reaction rates, thus allowing the detection of intermediate species and to rule out any gas-phase chemistry between the tin precursor and the oxygen source (water). X-ray photoelectron spectroscopy (XPS) was employed to detect surface species present and to rules out any gas-phase chemistry between the tin precursor and oxygen during the first stages of film growth. In this work, we will present our findings about these investigations and present a reaction mechanism, which is in good agreement with our XPS data.

II. EXPERIMENT

A. Substrate preparation

Si(100) wafers were cut into samples of 20*20 mm² and calcined in air at 750 °C for 24 h to grow a SiO₂ layer of several nanometers. After cooling down, the samples were placed in a 1:1 volumetric mixture of NH₄OH (25%) and H₂O₂ (35%) to remove carbon contamination and etch away the first monolayers of SiO₂. The mixture solution was stirred for 10 min, and then, the wafers were submerged into hot water (∼80 °C) for 30 min in order to fully hydrolyze the SiO₂ surface. Subsequently, wafers were blown dry with clean N₂ gas and brought into the vacuum (1 · 10⁻⁸ mbar) of the XP spectrometer for drying purposes. After drying, the samples were analyzed by XPS to confirm the quality of the cleaning procedure. TEM wafers used during experiments were labeled “5” and “15” as displayed in Table I. During these experiments, substrates were kept at room temperature (RT) or heated to 500 °C. After deposition, samples were transferred to the XPS using a stagnant vacuum transfer cell.

B. Low pressure reactor

Low pressure deposition experiments were carried out in a stainless steel (ultra) high vacuum (UHV) reactor, which was custom-build for this research project. Figure 1 shows a schematic representation of the reactor. The base pressure of the reactor (1 · 10⁻⁸ mbar) was maintained using a turbo pump and a liquid nitrogen cooled cryopump. Substrates inside the reactor could be heated to temperatures between room temperature and 600 °C. The gas-phase was monitored with a quadruple mass spectrometer (QMS). The substrates were transferred to and from of the reactor with a stagnant vacuum transfer cell.

C. MBTC deposition experiments

1. Adsorption of MBTC onto silica

After substrate preparation and XPS analysis, substrates were transferred to the low pressure reactor and exposed to pure MBTC vapor at a pressure of 5 · 10⁻⁶ mbar for time periods between 5 and 15 min (equal to 1150–3450 L). Experiments were labeled “5” and “15” as displayed in Table I. During these experiments, substrates were kept at room temperature (RT) or heated to 500 °C. After deposition, samples were transferred to the XPS using a stagnant vacuum transfer cell.

2. Sequential adsorption of MBTC and water at low pressure

Experiments with MBTC and water are similar to single component experiments apart from the water vapor step in between every MBTC vapor step. The water vapor step was kept constant for all experiments and consists of water vapor at a pressure of 5 · 10⁻⁶ mbar for 2 min (equal to 450 L) and was labeled “w” so that a sample made with 5 min MBTC vapor followed by 2 min of water vapor and again 5 min of MBTC vapor is labeled “5w5.” Detailed sample labeling can be found in Table I. During these experiments, substrates were kept at RT. After deposition, samples were transferred to the XPS using a stagnant vacuum transfer cell.

3. SnO₂ deposition by atmospheric pressure CVD

Atmospheric pressure CVD experiments were done using a stagnant-flow reactor connected to two bubblers containing MBTC and H₂O, heated to 125 and 40 °C, respectively, using oil baths. Details of this reactor set-up are described elsewhere. As substrate, silica TEM wafers were pretreated, transferred to the stagnant flow reactor, heated to 570 °C and exposed for 1 s to MBTC/H₂O vapor. After deposition, samples were analyzed by TEM.

D. X-ray photoelectron spectroscopy

XPS was measured with a Kratos AXIS Ultra spectrometer, equipped with a delay-line detector (DLD) and a monochromatic Al Kα x-ray source (Al Kα = 1486.6 eV) operating at 150 W. Spectra were recorded with a background pressure of 2 · 10⁻⁹ mbar and pass energies of 160 eV for survey scans and 40 eV for region scans. XPS measurements of the grafting experiments of SiO₂ were calibrated using the Si 2p signal of the SiO₂ wafer [Si 2p (SiO₂) = 103.30 eV (Ref. 15)]. Binding energies for Sn 3d were compared with the Sn 3d binding energy of a tin-butyl-containing polyhedral oligomeric silsesquioxane (Sn-POSS) reference compound (n-butyl-Sn-heptaisobutyl-POSS), which was synthesized in-house and described below (Fig. 2). XPS measurements of...
this Sn-POSS compound were calibrated using the Au 4f\textsubscript{7/2} signal of sputtered gold on the POSS material \[\text{Au 4f}_{7/2} (\text{Au}) = 84.00 \text{ eV} \text{ (Ref. 15)}\].

**E. Chemicals**

\(n\)-butyltin trichloride \((n\text{-C}_4\text{H}_9\text{SnCl}_3)\) (95%) was obtained from Aldrich and used as received. Diethyl ether and acetonitrile were all obtained from Biosolve and were dried using calcined alumina and molesieves, respectively. Ammonia (25%), hydrogen peroxide (35%), and triethyl amine (99%) were all obtained from Merck and all used as received, except triethyl amine, which was dried with KOH (Merck, 99%). Trisilanol-hepta-isobutyl-POSS \(((i\text{-C}_4\text{H}_9)\text{Si}_7\text{O}_9(\text{OH})_3)\) was kindly donated by Hybrid Catalysis BV and recrystallized in heptane (Biosolve, 99%) before use.

**1. Synthesis of \(n\)-butyl-Sn-heptaisobutyl-POSS (Sn-POSS)**

To a cooled \((-40 ^\circ \text{C})\) solution of \((i\text{-C}_4\text{H}_9)\text{Si}_7\text{O}_9(\text{OH})_3\) (24.70 g, 31.2 mmol) and liquid \(n\text{-C}_4\text{H}_9\text{SnCl}_3\) (9.45 g, 33.5 mmol) in dry diethyl ether (110 mL) was added triethyl amine (14.0 g, 138 mmol). The suspension was stirred overnight at RT and filtered to remove the majority of triethyl ammonium chloride. Acetonitrile (ca. 80 mL) was added to the filtrate, which was allowed to cool slowly to 0 \(^\circ \text{C}\). The solids were obtained by filtration, and washed with acetonitrile (ca. 50 mL), yielding the product (21.8 g, 22.6 mmol, 72%) as a white powder (mp \(= 217 ^\circ \text{C}\)) after vacuum drying.

\[\text{H-NMR (CDCl}_3\) \delta 1.847 (m, 7H, C\text{H} \text{isobutyl}) 1.759 (m, 3H, C\text{H} \text{3}), 1.449 (\text{sextet}, 3 \ J_{\text{HH}} = 7.4 \text{ Hz}, \text{C} \text{H}_2 \text{ butyl}), 26.15, 26.13 (\text{C}_2 + \text{C}_3 \text{ butyl}), 25.81, 25.78, 25.75, 25.68 (\text{CH}_3 \text{ isobutyl}), 24.15, 23.92, 23.91, 23.79 \text{ ppm.} \]

**FIG. 2.** (Color online) Reaction of different Si-OH groups with MBTC: (a) and (b) reaction of MBTC with silanol groups at the surface of etched SiO\textsubscript{2} wafer. (c) and (d) Reaction of trisilanol POSS with MBTC into \(n\)-butyl-Sn-heptaisobutyl-POSS.

**TABLE I.** Labeling of the low pressure experiments.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Minutes of exposure</th>
<th>minutes of MBTC exposure</th>
<th>minutes of H\textsubscript{2}O exposure</th>
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<td>15</td>
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<td></td>
</tr>
<tr>
<td>5w5w15</td>
<td></td>
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</tbody>
</table>

**FIG. 3.** (Color online) XPS analysis of the tin compounds: (a) XPS Sn 3d region scans of the \(n\)-butyl-Sn-heptaisobutyl-POSS and the grafted MBTC species on etched SiO\textsubscript{2} wafer at temperatures between RT and 400 \(^\circ \text{C}\). (b)–(d) Binding modes of the tin species observed during XPS analysis.
23.90, 23.54, 22.85, 22.60, 19.37 (Sn-CH2 butyl), 13.29 (CH3 butyl). MALDI-TOF (m/z): 791.32, 793.32 (i-C4H9)7Si7O9(OH)3, 963.32, 965.31 (Sn-POSS).

III. RESULTS AND DISCUSSION

A. Deposition from MBTC with and without H2O

Which group of the MBTC (alkyl or chloride groups) reacts first with the silica surface, i.e., which surface species are present during the formation of the SnO2 film? Figure 3 shows a series of Sn 3d spectra after adsorption of MBTC at substrate temperatures between RT and 500°C. Briefly, we conclude from these experiments that surface grafted Sn-butyl species, as depicted in Fig. 3(c), are present at room temperature. For temperatures of 50°C and higher, only Sn-hydroxy species, as in Fig. 3(d), were observed. Careful analysis reveals that MBTC adsorbed at silica below 50°C results in a Sn 3d5/2 peak with a binding energy of 487.28 ± 0.05 eV [Fig. 3(c)], which is very similar to the Sn 3d5/2 binding energy of 487.27 ± 0.05 eV of the reference compound n-butyl-Sn-heptaisobutyl-POSS (Sn-POSS) [Fig. 3(b)]. Open-cage POSS compounds are known as good models for surface silanol groups and therefore ideal as XPS reference compound, similar to the work of Nédez et al. who used Sn-POSS compounds as reference in nuclear magnetic resonance (NMR) and infrared (IR) spectroscopy.

Fig. 4. (Color online) Proposed reaction mechanism for MBTC and water on SiO2: (a) and (b) acid–base reaction of MBTC with silanol group; (c) removal of butyl group; (d) and (e) acid–base reaction of MBTC with Sn-OH groups. (f)–(i) systematic representation of the reaction mechanism in (a)–(e).

Fig. 5. (Color online) XPS Sn 3d analysis of samples made by multi-layer growth in the model-reactor using alternating dosing between MBTC and water. Samples (b), (c), and (d) are separately made samples with 1, 2, or 3 cycles of MBTC/water whereas sample (e) is made without the use of water but with the same deposition time as sample (d).
(1H-NMR and 13C-NMR) all confirm the structure of the n-butyl-Sn-heptaisobutyl-POSS (Sn-POSS) as the only compound present, and the fact that both Sn 3d5/2 binding energy values are identical, we believe in the presence of n-butyl-Sn-(O-Si)3 species anchored to the SiO2 substrate surface. This is also supported by binding energy values given by Behra et al. who measured sorbed MBTC on quartz sand.21 XPS analysis of adsorbed MBTC at SiO2 with substrate temperatures above 50 °C resulted in a Sn 3d5/2 peak at 487.48 ± 0.05 eV, which is about 0.2 eV higher than the binding energy for n-butyl-tin species discussed before. We suggest that this shift to higher binding energies is a result of a reaction of the n-butyl-Sn-(O-Si)3 species with small traces of residual water present in the reactor set-up and leads to the formation of HO-Sn-(O-Si)3 species as displayed in Fig. 3(d). To test this hypothesis, we did a room temperature experiment with MBTC followed by water and indeed the same binding energy shift of about 0.2 eV was observed. This mechanism of HO-Sn-(O-Si)3 formation is supported by binding energy values found in literature as Jiménez et al. investigated very thin SnO2 films on SiO2 and found a Sn 3d5/2 binding energy of 487.5 eV for an Sn-O-Si system.22 The same value is also found by Wang et al. during his research on SnO2 impregnated SiO2 spheres.23 Both groups explain this ~1 eV increase in binding energy compared with bulk SnO2 [Sn 3d5/2 (bulk SnO2) = 486.7 eV (Refs. 15 and 24)] by pointing toward interactions with the SiO2 and the first layers of SnO2. This effect of the electronegativity of atoms on binding energy values is described in more detail by Swartz et al.25 The results of these deposition experiments with MBTC are supporting our idea of an acid–base hydrolysis reaction mechanism without the need of gas-phase reactions. The lack of any evidence for grafted Sn-Cl species using XPS nor for a MBTC-H2O complex using mass spectrometry together with the fact that reaction of the tin precursor with the substrate is already possible at room temperature are strong indications that the Sn-Cl bonds in MBTC are highly reactive toward surfaces, without the need to invoke any secondary tin species, by radical chemistry or complexation of water molecules. Instead, we propose an acid–base hydrolysis reaction mechanism in SnO2 film growth similar to the reaction mechanism reported by Basset et al.12 and mechanisms reported for atomic layer deposition (ALD) processes.26–28 Figure 4 shows the different steps in our film growth mechanism: Figs. 4(a)–4(c) are based on the single component experiments described previously, and Figs. 4(d) and 4(e) are a repetition of the grafting and hydrolysis steps, but now Sn-OH groups are available for grafting instead of the Si-OH groups. A more schematic representation of this mechanism is shown in Figs. 4(f)–4(i).

**B. Depositions with MBTC and H2O**

In order to test the mechanism outlined above, we continued with multilayer film growth by alternating exposures of the substrate to MBTC and H2O. Figure 5 shows the XPS results of a series of multicomponent experiments using alternating MBTC and water steps. Figure 5(a) shows the XPS Sn 3d region of a clean SiO2 wafer, and Figs. 5(b)–5(d) show the XPS Sn 3d region of samples made with respectively zero (“5”), one (“5w5”) and two (“5w5w5”) water steps in between the MBTC steps (see Table I). The linear increase in
XPS signal indicates a step-by-step increase in deposited tin, which is in agreement with our film growth mechanism of Fig. 4. When MBTC reacts with surface hydroxyl groups and forms a layer of anchored butyl tin species, followed by a water vapor step, which converts the butyl groups into hydroxyl groups, one extra layer of tin is deposited. As a control experiment, we removed the water steps between the MBTC steps but left the MBTC deposition time unchanged ("15" instead of "5w5w5"). Without the water steps, the formation of surface hydroxyl groups should stop and further growth of the film should not be possible. This is indeed what happened. Figure 5(e) shows the XPS Sn 3d intensity of a sample made with a total exposure time of 15 minutes MBTC vapor ("15"). As the XPS Sn 3d signal intensity is equal to that of the 5 min sample [Fig. 5(b), "5"] and not to the 15 min sample [Fig. 5(d), "5w5w5"], we can conclude that the water steps between the MBTC steps are essential for the formation of surface hydroxyl groups—and so for film growth. This limitation effect between the precursor step and the oxidation step is commonly known as self-limiting or self-terminating growth, and is very common in ALD processes. To double-check this effect, we also did an experiment in which we first grow a film of three cycles MBTC and water and then separately exposed this film to 5 min MBTC vapor ("5w5w5w5") and 15 min MBTC vapor ("5w5w5w15"), respectively. The outcome was the same: both samples gave a linear increase in XPS signal equal to that of one monolayer of tin.

To compare the morphology of the SnO2 films produced in this study, we used specially designed TEM wafers employing electron transparent SiO2/SiNx membranes as described by us before. 13 We prepared two SnO2 films by sequential MBTC/H2O deposition in high vacuum (six cycles of MBTC/H2O and 12 cycles of MBTC/H2O) and compared these films with a film made with MBTC/H2O under APCVD conditions. Figure 6 shows some representative TEM results, with Fig. 6(a) showing a TEM image of the 6-cycle sample. In this sample, randomly distributed mostly SnOx particles were present with sizes around 3–4 nm. This was also true for the TEM images of the 12-cycle samples [Fig. 6(c)]. However, here we were able to find a small number of crystals with one of them displayed in Fig. 6(c). This crystal was about 20–30 nm in lateral dimensions and has a lattice spacing of 3.35 Å, which corresponds to the most intense SnO2 (110) reflection. 28 Even though we were able to resolve the lattice fringes of some large particles in the 12-cycle samples, all samples appeared completely amorphous in electron diffraction. For comparison, we also prepared a sample using a stagnant flow reactor with MBTC/H2O at 1 bar and a very short deposition of only 1 s. Figure 6(b) shows a TEM image of this sample and the first thing which can be observed is the similarity between the low pressure ALD-like sample of Fig. 6(a) and the APCVD-made sample of Fig. 6(b). This similarity supports the idea that both films were produced according to the same reaction mechanism, implying that only surface reactions are essential for film growth and no gas-phase reactions are needed since these reactions are very unlikely at pressures of 10⁻⁶ mbar.

IV. SUMMARY AND CONCLUSIONS

Based on our XPS and TEM results, we conclude that SnO2 films produced by APCVD are formed by direct adsorption of MBTC onto the film surface. We see no indication for gas-phase reactions playing any role of significance. We investigated the surface chemistry of MBTC and water at low pressure (10⁻⁶ mbar) and proposed an acid–base type of reaction mechanism, which fully describes our XPS findings. TEM analysis gave some insight into the first nucleation of film growth during ALD-like film growth, which was similar to the nucleation behavior observed in APCVD processes and supports our idea of the surface reaction-driven film growth.

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28 X. Meng, Y. Zhang, S. Sun, R. Li, and X. Sun, J. Mater. Chem. 21, 12321 (2011).