

Plasma-enhanced atomic layer deposition of WO₃-SiO₂ films using a heteronuclear precursor

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ABSTRACT

Tungsten oxide–silicon dioxide (WO_x–SiO_y) composite thin films were deposited for the first time via the remote oxygen plasma-enhanced atomic layer deposition (ALD) process using a novel metal-organic heteronuclear and heteroleptic precursor, bis(tert-butylimido)bis(trimethylsilylmethyl)tungsten. Self-limiting ALD growth was demonstrated over a wide temperature window of 203–328 °C with growth per cycle decreasing with increasing temperature from 0.75 to 0.4 Å/cycle, respectively. Residual gas analysis revealed ligand competition and showed that ligand reaction during ALD nucleation and growth was a function of deposition temperature, thereby affecting the film composition. As the temperature increased from 203 to 328 °C, the film composition [W/(Si + W)] ranged from 0.45 to 0.53. In addition, the carbon impurity content was reduced and the refractive index increased from 1.73 to 1.96, the density increased from 4.63 to 5.6 g/cm³, and the optical bandgap decreased from 3.45 to 3.27 eV. Grazing angle x-ray diffraction indicated that as-deposited films were amorphous. Upon annealing in O₂ at 500 °C or higher, depending on deposition temperature, films are crystallized into the triclinic WO₃ phase. At the same time, WO₃ is sublimed from the surface and films are reduced in thickness.

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I. INTRODUCTION

Tungsten oxide (WO₃) exists over a wide variety of temperature-dependent polymorphs, ranging from triclinic to about 17 °C, monoclinic from 17 to 350 °C, orthorhombic from 350 to 720 °C, monoclinic from 720 to 800 °C, and tetragonal from 800 to 900 °C.¹ Originally used in tungsten bronzes for its pigmentation properties, WO₃ also exhibits interesting electrochromic, photochromic, oxygen vacancy conduction, and catalytic properties. When combined with SiO₂, WO₃–SiO₂ composite films are of great interest for emerging applications in olefin catalysis,² interference filters,³ and high sensitivity gas sensors.^{4,5} Popular methods of synthesizing WO₃–SiO₂ composites include spin-coating,⁶ aqueous precursor impregnation,⁷ aerosol-assisted solgel,⁸ and ink-jet printing.⁵ Although some of these techniques have produced good quality films, emerging applications in catalysis and coatings

require a conformal and uniform coating of either nanoparticles or high aspect ratio structures over large wafer areas, respectively. Atomic layer deposition (ALD), based on the repeating cycles of purge-separated self-limiting surface reactions, is one of the few techniques capable of depositing ultrathin films conformally and uniformly over large surface areas with angstrom level thickness control. The traditional approach to deposit WO₃–SiO₂ composites via ALD would involve the use of super-cycles with alternating cycles of the binary ALD processes of interest [i.e., one or more ALD cycle(s) of WO_x followed by one or more of SiO_x]. In this scenario, the choice of precursors (both reactants and co-reactants) is paramount to avoid unexpected growth rates and film compositions that might result from nucleation effects and ligand interactions between each binary ALD process.⁹ While a recent review by Vasilev *et al.* provides an overview of binary ALD processes involving the deposition of SiO₂,¹⁰ a similar review on precursors to deposit WO_x is lacking.

Summarized in Table I are literature reports on the ALD synthesis of WO_x . The first attempts at depositing WO_3 via ALD followed the footsteps of successful CVD processes and used halide precursors.^{11,12} The first report of ALD WO_3 used WF_6 with H_2O as the oxygen source.¹³ However, WF_6 was found to adsorb poorly onto oxide surfaces with very little nucleation. The use of H_2O plasma as an oxygen source for WF_6 was later shown to aid film growth, producing WO_3 films over temperatures ranging from 30 to 180 °C.¹⁴ To enhance nucleation and develop a viable ALD process, attempts were made to increase reactivity using *in situ* synthesized oxy-halides such as WO_xF_y (Ref. 13) and WOCl_4 .¹⁵ In general, however, the halide and oxy-halide precursors were found to generate corrosive by-products such as HF and HCl. Associated drawbacks such as increased risk of self-etching,^{13,14} long pulse durations to achieve saturation,¹⁴ and residual F and Cl in as-deposited films^{13,15,16} prompted the need for alternative tungsten precursors.

Hexacarbonyl $[\text{W}(\text{CO})_6]$ as an alternative to halides was first investigated by Malm *et al.*,¹⁷ who used O_3 as the oxidizer and reported uniform growth of an amorphous film over a narrow temperature window of 195–205 °C with a growth per cycle (GPC) of 0.2 Å/cycle but did not report self-limiting saturation. Post-deposition annealing at 600–1000 °C in either O_2 or N_2 improved film crystallinity but increased film RMS roughness. A similar process, with 600 °C annealing, later yielded similar films.¹⁸ Alternative $\text{W}(\text{CO})_6$ processes using H_2O_2 or H_2O as co-reactants required higher deposition temperatures to achieve a similar GPC and resulted in high levels of incorporated carbon, which was not improved upon postdeposition annealing as the incorporated carbon tended to form W–C bonds upon annealing.^{19,20} In addition, the H_2O_2 process showed no evidence of saturation, although this was attributed to the long pulse times required to coat powdered TiO_2 nano-particle substrates.¹⁹ Overall, ALD processes involving $\text{W}(\text{CO})_6$ showed at best narrow temperature windows,¹⁷ and high levels of carbon incorporation, with thermal decomposition occurring at above 325 °C and partial decomposition when held for extended periods of time (>1 month) at 80 °C.¹⁹

To overcome the deficiencies of halide and carbonyl precursors and to target wider ALD windows, a recent focus in ALD WO_3 process development has been the exploration of novel metal-organic tungsten precursors. The first report of ALD WO_x using a metal-organic precursor was by Dezelah *et al.* who used $\text{W}_2(\text{NMe})_6$ and H_2O to demonstrate the influence of the metal oxidation state on film stoichiometry, showing that the +3 oxidation state of tungsten in $\text{W}_2(\text{NMe})_6$ resulted in the first reported synthesis of W_2O_3 films using ALD.²¹ A similar influence of the oxidation state on stoichiometry was later reported by Song *et al.* using $\text{WH}_2(\text{iPrCp})_2$, a +4 oxidation state precursor, with O_2 plasma.²² The resulting film was reported to have a net O/W stoichiometry of 2.4, possibly due to a mix of the $\text{W}4\text{f}^{+4}$, $\text{W}4\text{f}^{+5}$, and $\text{W}4\text{f}^{+6}$ oxidation states, resulting from the initial reduced state of the precursor in the metal-organic complex. However, precise control over stoichiometry was not achieved.

One of the most widely investigated tungsten precursors is bis(*t*-butylimido)bis(dimethylamino)tungsten (BTBAW). Liu *et al.* used BTBAW with H_2O to synthesize WO_x films and saw that GPC increased from 0.2 to 1.0 Å/cycle as the temperature increased

between 300 and 350 °C.²³ Relatively long H_2O pulses were necessary to initiate the growth of WO_3 , indicating the reaction of BTBAW with H_2O to be slow.^{23–25} Subsequent reports of BTBAW/ H_2O processes found a similar temperature trend, albeit with a slight difference in reported GPC values, possibly due to different reactor configurations.^{15,24} While both Liu *et al.* and Zhuiykov *et al.* reported the self-limiting behavior of the ALD reaction up to 350 °C, Bergum *et al.* attributed a sudden rise in GPC at 350 °C to the onset of CVD.¹⁵ The onset of CVD is consistent with the onset of a significant exotherm at 350 °C (see Fig. S1 in the supplementary material),²⁶ which indicates a decomposition component, BTBAW, at this temperature. Li *et al.* reported the first use of O_2 plasma with BTBAW to synthesize WO_3 at 150 °C.²⁷ Using the same BTBAW/ O_2 plasma combination, Balasubramanyam *et al.* later reported self-limiting saturating ALD growth over a substrate temperature range of 91–285 °C.²⁸ For films as-deposited at a substrate temperature of 285 °C, they saw the monoclinic phase of WO_3 and a film density of 5.9 g/cm³, significantly lower than that of bulk crystalline WO_3 (~7.3 g/cm³), which they attributed in part to ligand incorporation. WO_3 films were also deposited using BTBAW and O_2 plasma at 40 and 300 °C by Chen *et al.*²⁹ WO_x films with void fractions as high as 70–80% have been reported recently by Kilic *et al.*³⁰ who used BTBAW, H_2O , and O_2 plasma as co-reactants in an ABC-type process at a relatively high deposition temperature of 430 °C, which may have resulted in ligand incorporation through decomposition (see Fig. S1 in the supplementary material).²⁶ Zhao *et al.* later used BTBAW and O_2 plasma at 300 °C followed by annealing at 450 °C for 1 h in either synthetic (1:4 O_2 : N_2) air, O_2 , or N_2 .³¹ Oxygen vacancy content in WO_3 , assessed using x-ray photoelectron spectroscopy (XPS), was found to decrease with increasing O_2 partial pressure. Finally, a recent ALD study using BTBAW and various co-reactants at 350 °C revealed that using stronger oxidizers, such as NO_2 or O_3 when compared to H_2O , O_2 , or $\text{H}_2\text{O}_2/\text{H}_2\text{O}$, more effectively cleaved W–N bonds and resulted in a lower impurity content.³² However, as-deposited films synthesized using NO_2 were still found to be less dense (5.62 g/cm³) than bulk WO_3 , which was attributed to a mixture of amorphous and polycrystalline WO_3 phases.

A few other metal organic precursors have also been investigated. Mouat *et al.* attempted to synthesize WO_3 films that were intentionally porous using $\text{WO}_2(\text{tBuAMD})_2$, a high steric hindrance precursor. Various co-reactants were investigated, but with the exception of H_2O , they resulted in little to no film growth. Using H_2O , low-density (3.58 g/cm³), porous films were synthesized, which were crystallized into porous WO_3 nanowires upon annealing in air for 6 h at 500 °C.³³ Mattinen *et al.*, using the heteroleptic imino-amidinato tungsten complex $[\text{W}(\text{tBuN})_2(\text{dpamd})_2]$ and O_3 , reported a steady increase in the GPC of WO_3 from 0.2 to 0.6 Å/cycle for temperatures ranging from 200 to 350 °C.³⁴ The density and refractive index were found to increase significantly with increasing deposition temperature, with a near bulk density of ~7.4 g/cm³ reported for films deposited at 350 °C. However, evidence of precursor decomposition was observed for a temperature of 325 °C and above. Interestingly, improvement in film crystallinity was observed by increasing the number of cycles as well as the pulse length of O_3 .

TABLE I. Summary of ALD WO_x processes reported in the literature. As-deposited films synthesized were amorphous unless otherwise indicated. The deposition “windows” in this table include temperatures at which GPCs were reported and do not necessarily imply the actual substrate temperature or self-limiting growth. Phase of the precursor reported at room temperature and pressure.

Tungsten prec. (phase, ox. state)	Prec. temp. (°C)	Co-reactant	Substrates used	Deposition window (°C)	GPC (Å/ cycle)	O/W ^a	Post-dep. anneal	Crystal phase (as-dep; anneal)	RL, ρ (g/cm ³) E_g (eV)	Ref.
i. WF_6 ii. WO_3F_2 , (gas, +6)	200–600 ^d	i, ii. H_2O	i, ii. Sapphire (000112)	i, ii. 200	i. <0.1 ii. 0.2–0.8	ii. 3.0	—	ii. M; —	—	13
WF_6 (gas, +6)	—	P- H_2O Si_2H_6	Si (111) Hematite (0001)	30–180 ^c 200 ^b	0.2–0.45 1/3 ML	— 2.85 i. 3.0 ii. 2.28	— i. O_2 : 350 °C ii. 2% H_2/He : 350 °C	A; — —	p: 3.6–3.8 ^f —	14 16
WOCl_4 (solid, +6)	100–180	H_2O	i. Si ii. Mg iii. Pd iv. La_2O_3 V Al_2O_3	i–v. 150–300	i–iii. — iv, v. 1–2 ML	—	—	—	—	15
$\text{W}(\text{CO})_6$ (solid, +6)	23	O_3	Si (100)	160–250 ^{b,g}	0.05–0.4	3.0	i. O_2 : 600–1000 °C ii. N_2 : 600– 1000 °C	A; i, ii. T	—	17
—	—	O_3	Si (111)	190	0.21	3.0	Air: 600 °C	A; M (600 °C)	E_g : 3.5	18
80 ^c	80 ^c	H_2O_2	TiO_2 nano-particles	180–200 ^b	—	—	Air: 200–500, 750 °C	A; —	p: 7.16	19
70 ~120	70 ~120	H_2O H_2O	Si (100) Si (100)	300 140–240	0.2 1.2–2.0	— 1.46–1.39 ^b	Air: 500–700 °C	A; M	E_g : 3.28	20 21
$\text{W}_2(\text{NMe})_6$ (solid, +3)	95 ^c	P- O_2	SiO_2/Si	300	0.9	2.4	H_2S : 1000 °C ^j	—	—	22
$\text{WH}_2(\text{tPrCp})_2$ (solid, +4)	75	H_2O	ITO, TiSi_2	300–350	0.2–1.0	3.0	O_2 : 550 °C	A; M	—	23
60 ^c — 80 100 50 ^c	60 ^c — 80 100 50 ^c	H_2O H_2O H_2O P- O_2 P- O_2	Si, Mg, Pd SiO_2/Si SiO_2/Si Quartz Si	275–375 ^{b,j} 300–350 350 ^b 150 ^b 100–400 ^k	0.07–0.6 0.2–0.9 1–2 ML 1.08 0.68–0.43	— 3.0 3.0 — 2.9	600 °C Air: 200, 400 °C Yes CS_2 : 700 °C ^j —	A; — A; — — — M (400 °C); —	— — — — RL: 2.1–2.2 p: 5.8–5.9 E_g : 3.12–3.23	15 24 25 27 28
30 ^c 80 50 ^c	30 ^c 80 50 ^c	P- O_2 $\text{H}_2\text{O}/\text{P}-\text{O}_2$ P- O_2	Fused silica p-Si (100) FTO	40 ^b 300 ^b 430 300	0.6 0.9 —	— 2.86 i. 2.96 ii. 2.95 iii.	H_2S : 650, 850 °C ^j — i. Air: 450 °C ii. N_2 : 450 °C iii. O_2 : 450 °C	— M; — A; i–iii. M	— — E_g : i. 3.0	29 30 31
i. 75 ii–iv. 25	i. 75 ii–iv. 25	i. NO_2 ii. $\text{H}_2\text{O}_2/\text{H}_2\text{O}$ iii. O_2 iv. O_3	i–iv. Si	i–iv. 350 ^j	i. 0.7 ii. 0.52 iii. 0.42 iv. 0.22	i–iv. 2.9– 3.0	i–iv. Ar: 500 °C	i–iv. T/TR; —	p: i–iv. 5.62	32
150	150	i. H_2O ii. O_2 iii. O_3 iv. $\text{H}_2\text{O}/\text{O}_2$ v. O_2/O_3 vi. TMA vii. Si_2H_6	i–vii. n-Si (100)	i–vii. 250	i. ~0.14 ii– vii: —	i. 3.0 i–vii: —	i. Air: 500 °C, ii–vii. —	i. A; M/O, ii–vii: —	RL: i. 1.21, p: i. 3.58, E_g : i. 3.64 ^{PA} , ii–vii.	33
155	155	i. O_3 ii. H_2O	i, ii. Si. soda-lime	i, ii: 200–350 ^m	i. 0.2–0.6, ii. —	i. ~2.95, ii: —	—	i. A(M ⁿ); —, ii: —	RL: i. 1.8–2.3; p: i. 5.7–7.4, ii: —	34

TABLE I. (Continued.)

Tungsten prec. (phase, ox. state)	Prec. temp. (°C)	Co-reactant	Substrates used	Deposition window (°C)	GPC (Å/ cycle)	O/W ^a	Post-dep. anneal	Crystal phase (as-dep; anneal)	RI, ρ (g/cm ³) E_g (eV)	Ref.
WH ₂ (Cp) ₂ (solid, +4)	130	i. RP-O ₂ ii. RP-O ₂ /H ₂	i. ii., Al ₂ O ₃ /Si	i. 175–325, ii. 300	i. ii., 0.4–0.9	i. 3.0–2.98, ii. 2.94– 2.88	—	i. M; —, ii. —	RI: i. 1.99– 2.01, ii. —	35
W(tBuN) ₂ (Me ₃ SiMe) ₂ (liquid, +6)	130	O ₃	SiO ₂ /Si, sapphire (0001)	300	1.1	2.98–3.0	—	M; —	ρ : 7.2	36
	110	RP-O ₂	Si (100), TiN, TaN	120–370	1.0–0.45	3.0	O ₂ ; 400–600 °C	A; T	RI: 1.73–1.94, ρ : 4.63–6.16, E_g : 3.45–3.27	This ^o work

^aO/W ratio reported using XPS, EDS, and/or TOF-ERDA analyses for films as-deposited.

^bDo not report self-limiting growth; A—amorphous; T—triclinic; TR—tetragonal; M—monoclinic; O—orthorhombic; FTO—fluorine-doped tin oxide; Cp—cyclopentadienyl; iPr—isopropyl; tBuAMD—N,N'-di-tert-butylacetamidate; dpamd—N,N'-diisopropylacetamidate; P-O₂—O₂ plasma; P-H₂O—H₂O plasma; RP-O₂—remote O₂ plasma; ML—monolayer.

^cReport self-etching at 180 °C.

^dSubstrate at 200 °C.

^eBubbler.

^fReport ρ = 8.2 g/cm³ for films deposited at 60 °C.

^gReport high non-uniformity at 250 °C.

^hReported over temperature range (160–200 °C)

ⁱCVD above 350 °C.

^jFor the synthesis of WS₂.

^kSubstrate temperature (91–285 °C).

^lGPC investigations at 300 and 400 °C showed little growth and CVD, respectively; PA—post-anneal.

^mOnset of decomposition reported at 325 °C.

ⁿMonoclinic reported for >325 °C.

^oReport WO_x-SiO_y composite films.

Composition control is of interest for the use of WO_3 in emerging memory applications, where control over oxygen vacancy concentration is desirable for improving device performance and reliability. Romanov *et al.* and Kozodaev *et al.* showed the modulation of oxygen vacancy concentration, V_{O} , using $\text{WH}_2(\text{Cp})_2$ with various oxidizing agents. Romanov *et al.*, using remote plasma, reported the control of V_{O} in ALD WO_3 films using (1) deposition temperature, (2) O radical exposure time, and (3) H radical post-treatment exposure time in an “ABC” type process using $\text{WH}_2(\text{Cp})_2$ with separate O_2 and H_2 plasma exposure steps.³⁵ The greatest range of control was achieved using scenario (3) at a deposition temperature of 300 °C. Film resistivity and V_{O} (assessed using XPS) were found to increase weakly with increasing deposition temperature, decreasing O radical exposure time ($>10^6$ – $12.5 \text{ } \Omega \text{ cm}$), increasing H^* exposure time (down to $1.1 \text{ } \Omega \text{ cm}$), and decreasing film crystallinity. Higher deposition temperatures were not possible due to the onset of CVD at 325 °C. Kozodaev *et al.* reported an increase in film monoclinic WO_3 crystallinity and a decrease in V_{O} (assessed using XPS) with an increase in the O_3 dose.³⁶

Despite all this work, there remains a need for a room temperature liquid metal-organic tungsten precursor with a wide ALD temperature range. To date, there have been no reports of the synthesis of WO_3 – SiO_2 composite films via ALD. An alternative and perhaps simpler approach to synthesizing WO_3 – SiO_2 composites via supercycles would be to use a heteronuclear precursor (containing both tungsten and silicon).⁹

In this work, we report the first single precursor PEALD process for WO_3 – SiO_2 using a new heteronuclear metal organic precursor, bis(tert-butylimido)bis(trimethylsilylmethyl)tungsten (referred to as BITSW) and O_2 plasma. BITSW is a liquid at room temperature (the only other liquid tungsten precursor is BTBAW) and is stable up to 400 °C, among the highest of any metal organic tungsten precursor to date. Nucleation, saturation, and growth behavior were investigated on Si as well as metals such as TiN and TaN. Reaction mechanisms were investigated using *in situ* residual gas analysis. Crystallinity, density, roughness, and composition were investigated in as-deposited and O_2 annealed films using XPS, x-ray diffraction (XRD), x-ray reflectivity (XRR), and spectroscopic ellipsometry (SE).

II. EXPERIMENT

ALD was performed in a Picosun Sunale R-200[®] PE-ALD reactor using $\text{W}(\text{tBuN})_2(\text{CH}_2\text{SiMe}_3)_2$ (abbreviated as BITSW) as the tungsten source and O_2 plasma as the oxygen source with N_2 and Ar carrier gases, respectively. BITSW was held at 110 °C using a Picobooster ampoule. O_2 plasma was generated using a Litmus RPS 2800 W remote plasma source. A pulse sequence of 2/15/60/30 s (BITSW/ N_2 purge/ O_2 plasma/ N_2 purge) was used unless otherwise specified. The reaction chamber was maintained at a pressure of 100 Pa during depositions with the hot-wall of the chamber at the deposition set-point temperature, T_{WALL} . The chamber was allowed to thermally settle for 60 min prior to the start of each run. The difference between T_{WALL} and the actual temperature seen on the substrate, T_{DEP} , was calibrated using a SensArray 1770 process probe wafer (see Fig. S2 in the supplementary material).²⁶ T_{DEP}

will be used throughout the rest of the paper, unless otherwise specified. Reaction by-products during ALD cycling were analyzed using a Stanford Research Systems residual gas analyzer (RGA) operating at room temperature and a base pressure of 3.4×10^{-7} kPa while exposed to the reaction chamber. Thermogravimetric analysis (TGA) of BITSW was performed in a TA Instruments model Q50 under an N_2 atmosphere at atmospheric pressure with a ramp rate of 10 °C/min. A Mettler-Toledo 822e was used to acquire closed cup, power compensated differential scanning calorimetry (DSC) data for BITSW under an N_2 atmosphere. DSC temperature ramps were performed from 0 to 400 °C with a ramp rate of 5 °C/min using an HP gold pan.

WO_x – SiO_y films were deposited on three types of $2 \times 2 \text{ cm}^2$ (100) Si coupons: (1) native oxide/Si, (2) 100 nm TiN/100 nm SiO_2 /Si, and (3) 20 nm TaN/100 nm SiO_2 /Si. Film thickness and optical constants were characterized using spectroscopic ellipsometry performed on a J.A. Woollam M2000 over a photon energy range of 1.27–5.16 eV and modeled using COMPLETEASE 6.0 software. First, the thickness of the WO_x – SiO_y films, $d_{\text{WO}_x\text{--SiO}_y}$ (nm), deposited on Si [coupon type (1)] was extracted by fitting a Cauchy layer on top of a 1.5 nm native SiO_2 layer for photon energies below 3.0 eV (where the WO_x – SiO_y film is transparent). Next, the refractive index and extinction coefficient were extracted for 300 cycle WO_x – SiO_y films at each deposition temperature by fitting a spline layer using the Cauchy extracted $d_{\text{WO}_x\text{--SiO}_y}$ and an initial n of 2.1 (commonly reported for ALD WO_3 films),^{28,37} followed by a Tauc–Lorentz oscillator parameterization to ensure Kramer–Kronig consistency. Similarly, the optical constants for the TiN and TaN substrates used in this study were modeled using the Lorentz oscillators, followed by the Cauchy layer modeling of the overlying deposited WO_x – SiO_y films.

Post-deposition annealing at ambient pressure in O_2 was performed in a 2 in. diameter Carbolite quartz tube furnace at various anneal temperatures for 1 h. Prior to each anneal, the quartz tube was first purged of air and moisture using a 20 SCCM O_2 flow for 1.5 h at 130 °C, followed by ramping up to the anneal temperature at a rate of 15 °C/min. Following annealing, the tube was allowed to cool naturally with the same O_2 flow to a temperature of 120 °C before unloading samples.

To assess the crystallinity of as-deposited and annealed films on Si, grazing incidence x-ray diffraction (GI-XRD) measurements were performed at room temperature using a Rigaku Ultima IV x-ray diffractometer equipped with a $\text{Cu K}\alpha$ x-ray source. GI-XRD scans were performed at an angle of incidence, $\omega \sim 0.5^\circ$, slightly above the critical angle for the WO_x films used in this study. Mass density (g/cm^3), $d_{\text{WO}_x\text{--SiO}_y}$, and RMS roughness (nm) for these films were extracted using XRR measurements performed on the same tool at room temperature using models developed in GlobalFitTM.

The composition of the WO_x – SiO_y films synthesized in this study was analyzed using XPS, performed using a Thermo Scientific ESCALAB 250Xi system with a 50 W Al $\text{K}\alpha$ source on 40 nm thick films at a take-off angle of 58°. Photoelectrons emitted from the approximately top 2 nm of the film are detected. A pass energy of 50 eV and an analysis area with a 400 μm spot diameter were used. The acquired spectra were subsequently fitted with component peaks using CASAXPS software, with peak binding energies

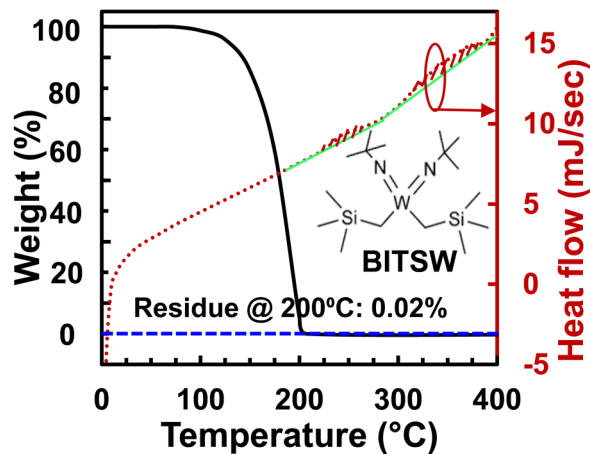


FIG. 1. TGA weight loss (solid line) and PC-DSC (dotted line) scans of BITSW vs temperature collected in separate measurements and combined on the axes for ease of comparison.

referenced to a 284.8 eV aliphatic adventitious carbon peak. All acquired spectra were corrected for Shirley background, except for C1s spectra, where a linear correction was found to be appropriate. Quantitative atomic percentage analysis was performed after Ar ion sputtering at 2 keV for 10 s (at a sputter rate of 0.26 nm/s) to remove adventitious carbon. Survey spectra were acquired with a pass energy of 150 eV.

III. RESULTS AND DISCUSSION

A. Precursor characterization

Shown in Fig. 1 is the TGA plot of percent weight loss versus temperature for BITSW. A steep one-step weight loss starting at around 150 °C with negligible residue above 200 °C indicates a clean evaporation profile, desirable for an ALD precursor. Shown on the secondary y-axis is a closed-cup power-compensated

differential scanning calorimetry (PC-DSC) scan of heat flow versus temperature, collected using a different instrument. Upon ramping the temperature of the precursor to 400 °C, two regions of exothermic behavior were observed as the deviation of the measured heat flow against a fitted linear baseline (solid green lines): (1) a mild exotherm starting at ~220 °C reaching maximum intensity at 250 °C and (2) a larger exotherm starting at ~325 °C, reaching maximum intensity at around 350 °C. In deposition trials, BITSW was found to be stable up to at least 328 °C, as will be discussed later.

B. ALD process and as-deposited film characterization

Shown in Fig. 2(a) are the plots of $d_{\text{WO}_x\text{-SiO}_y}$ (extracted from SE) versus number of ALD cycles for depositions on Si substrates at growth temperatures ranging from 120 to 370 °C. The SE thickness was found to correlate with the $\text{WO}_x\text{-SiO}_y$ thickness modeled from XRR data (see Fig. S3 in the supplementary material).²⁶ Film GPCs were determined from the slope of linear fits, with $R^2 > 0.99$ over the entire temperature range. Little to no nucleation delay was seen for films deposited on Si at temperatures up to 370 °C. Plots of GPC, refractive index measured at 1.95 eV (633 nm), and density (g/cm^3) versus T_{DEP} are shown in Fig. 2(b). The GPC generally decreased from 1.0 Å/cycle at 120 °C to ~0.4 Å/cycle at 328 °C, with a relatively constant GPC of around 0.4 Å/cycle in a temperature window between 266 and 328 °C. An increase in GPC to ~0.5 Å/cycle at 370 °C is likely due to a parasitic CVD component resulting from the thermal decomposition of BITSW on or near the surface of the wafer and correlates with the exotherm seen at 350 °C (Fig. 1). The decreasing GPC between 120 and 328 °C was accompanied by significant increases in both the refractive index and the density, from 1.73 to 1.96 and 4.63 to 5.6 g/cm^3 , respectively. While refractive index and density values are lower than those of single crystal bulk triclinic WO_3 (2.45 and ~7.3 g/cm^3 , respectively),^{38,39} they are higher than those of amorphous SiO_2 (1.45 and 2.2 g/cm^3 , respectively).⁴⁰ These values are in agreement with values reported for WO_x thin films deposited via ALD in the temperature range of 100–350 °C.^{28,32,34} We observed similar growth behavior for films deposited on TiN and TaN, as discussed

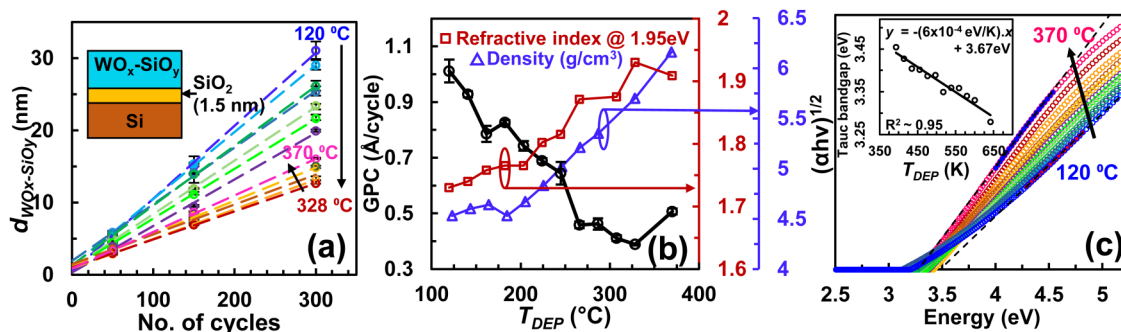


FIG. 2. Plots of (a) $d_{\text{WO}_x\text{-SiO}_y}$ vs number of ALD cycles for various T_{DEP} ; (b) GPC (circles), refractive index measured at 1.95 eV (squares), and density (triangles) vs T_{DEP} for films deposited on Si; (c) Tauc plots for 300 cycle films with the dashed lines indicating linear fits for the 120 and 370 °C samples. The inset shows a plot of Tauc E_g vs T_{DEP}

in further detail in the supplementary material (Fig. S4 in the supplementary material).²⁶

The optical bandgap for the as-deposited films was assessed using the Tauc method and the following relation:

$$(\alpha h\nu)^{1/\gamma} \propto h\nu - E_g, \quad (1)$$

where α is the absorption coefficient (cm^{-1}), h is the Planck constant (in eV s), ν is the frequency of incident light (Hz), and E_g is the Tauc bandgap (in eV). γ is chosen to be equal to 2, assuming an indirect transition.⁴¹ Shown in Fig. 2(c) are the Tauc plots of $(\alpha h\nu)^{1/2}$ vs $h\nu$ for 300 cycle films. Linear extrapolation of these plots to the x-axis yielded the E_g of the $\text{WO}_x\text{-SiO}_y$ films at each deposition temperature. The inset in Fig. 2(c) shows the extracted E_g plotted vs T_{DEP} (in K). For T_{DEP} increasing from 350 to 650 K, E_g was found to decrease roughly linearly from 3.45 to 3.21 eV. Similar reports of an inverse linear relationship of E_g vs deposition temperature in nanocrystalline WO_3 films ascribed it to quantum confinement.^{37,42} A linear fit of these data yielded a temperature coefficient of ~ -0.0006 eV/K and a y-intercept of 3.67 eV (an estimate of the optical bandgap at 0 K), similar values to those reported for amorphous WO_3 .⁴³ All of these values are larger than the E_g reported for single crystal bulk triclinic WO_3 (~ 2.62 eV) but smaller than that of amorphous SiO_2 (~ 9 eV).^{44,45} However, as WO_3 has a smaller bandgap, it will dominate optical absorption.

The hallmark of an ALD process lies in the self-limiting nature of the reaction of half-cycles. Figure 3 shows the plots of SE thickness versus (a) BITSW and (b) O_2 plasma pulse times for 150 ALD cycle films deposited at 203 and 328 °C. BITSW exhibited saturation for pulse lengths as short as 0.1 s at 203 °C and between 3

and 4 s at 328 °C. The remote O_2 plasma source used in this study requires long exposure times to deliver sufficient O radical flux to the wafer. Consequently, much longer O_2 plasma pulse times of 60 and 40 s were required for growth saturation at 203 and 328 °C, respectively. The observation of saturation for exposure to both reactants indicates a self-limiting ALD process over a wide temperature range (203–328 °C). This also suggests that the mild exotherm seen in the DSC scan starting at ~ 220 °C (see Fig. 1) may not be a decomposition event or might be a small decomposition event not significant enough to affect ALD saturation.

$\text{WO}_x\text{-SiO}_y$ SE thickness uniformity maps over 150 mm diameter silicon wafers for 300 cycle films deposited using a pulse sequence of 2/15/60/30 s are shown in Fig. 3 for films deposited at (c) 203 and (d) 328 °C. Film non-uniformity, calculated as the ratio of the standard deviation to the mean film thickness, was found to be $\sim 6.7\%$ for 203 °C, slightly improving to $\sim 5\%$ at 328 °C, indicating reasonable thickness uniformity over a large area.

C. Post-deposition O_2 annealing

In an attempt to improve film properties and induce crystallization, *ex situ* post-deposition isochronal annealing was performed sequentially on the same samples at temperatures of 400, 500, and 600 °C for 60 min in O_2 . Comparisons of GIXRD scans for as-deposited and annealed films are shown in Fig. 4 for 300 cycle films deposited at (a) 203 and (b) 328 °C. As-deposited films were consistent with nano-crystalline WO_3 , displaying broad peaks at $2\theta \sim 23.6^\circ$ and $\sim 55^\circ$, with a Scherrer crystallite size of < 1 nm for the $\langle 002 \rangle$ peak. After annealing at 600 °C, all films were crystallized into the triclinic phase of WO_3 (JCPDS Card No. 020-1323), generally reported for WO_3 films near room temperature.¹ The expected orthorhombic phase for WO_3 was not seen upon annealing at 600 °C as it could not be retained upon cooling the films to room temperature (where GIXRD scans were acquired).⁴⁶ Scherrer analysis of the $\langle 002 \rangle$ peak suggests an average grain size of about 6–7 nm for both 203 and 328 °C films following 600 °C annealing (see Table SI in the supplementary material).²⁶ The 328 °C films showed weak crystallization even after annealing at 500 °C, as indicated by the appearance of the $\langle 002 \rangle$ and $\langle 202 \rangle$ peaks. Subsequent annealing of these films at 600 °C resulted in crystallite growth, as indicated by a sharpening of the full width at half maximum (FWHM) of the $\langle 002 \rangle$ and $\langle 202 \rangle$ peaks and the appearance of additional WO_3 peaks. Film thickness ($d_{\text{WO}_x\text{-SiO}_y}$ is thickness measured using XRR) also decreased with increasing anneal temperature, as discussed further below. The lower crystallization onset temperature of the 328 °C films, taken with the reduced GPC, suggests reduced impurities.

D. Elemental analysis and nucleation study

1. XPS

Figure 5 shows XPS elemental analysis of tungsten, silicon, and oxygen on 40 nm thick films as-deposited using 700 and 1300 cycles at 203 and 328 °C, respectively, and subsequently isochronally annealed at atmospheric pressure for 60 min in O_2 at 400, 500, and 600 °C. Core level spectra of tungsten for films as-deposited and after the 600 °C anneal are shown in Figs. 5(a),

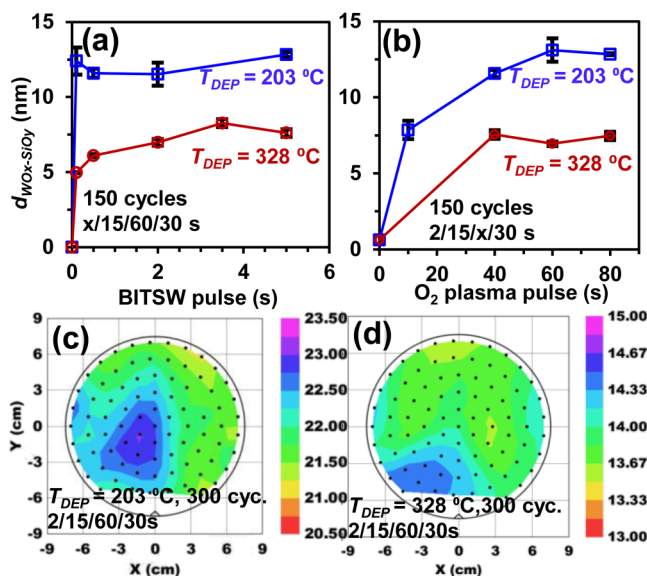


FIG. 3. Saturation plots of $d_{\text{WO}_x\text{-SiO}_y}$ vs (a) BITSW and (b) O_2 plasma pulse times for $T_{\text{DEP}} = 203$ and 328 °C with other pulse times fixed. $\text{WO}_x\text{-SiO}_y$ thickness uniformity maps for 300 cycle films deposited at (c) 203 and (d) 328 °C.

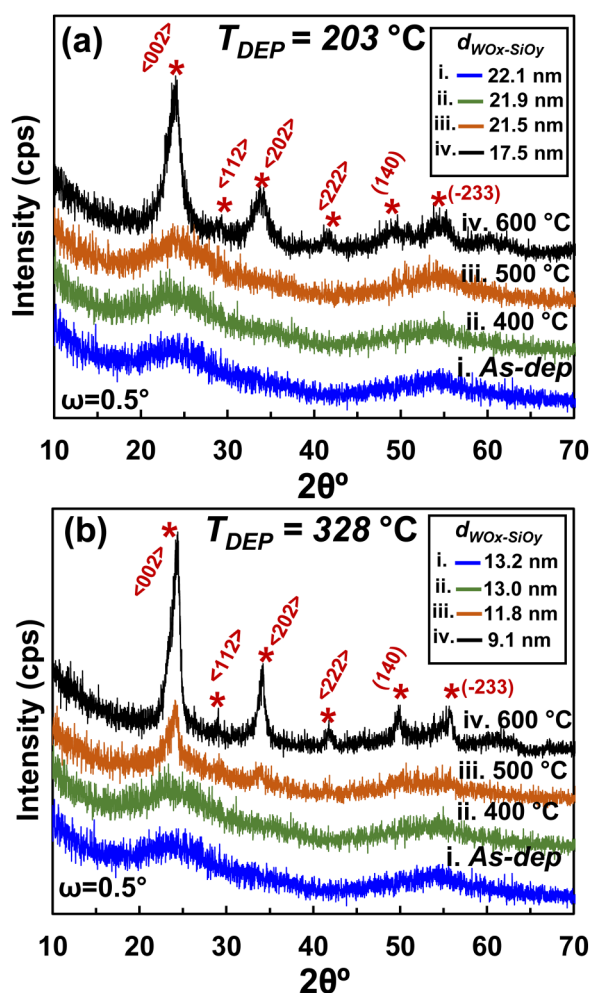


FIG. 4. GIXRD scans comparing films deposited at (a) 203 and (b) 328 °C and following isochronal annealing. The peaks indicated by an "*" are referenced to the triclinic phase of WO_3 (JCPDS Card No. 020-1323).

5(d), 5(g), and 5(j). Tungsten 4f core-levels fitted using a doublet feature showed $\text{W}4f_{7/2}$ and $\text{W}4f_{5/2}$ peaks at a binding energy of ~ 36.0 and 38.2 eV, respectively. Along with a tungsten $5p_{3/2}$ peak at ~ 41.8 eV, their presence suggests tungsten in the form of WO_3 in all as-deposited and O_2 annealed films.^{47,48}

Oxygen O1s core-level peak fitting for the as-deposited films [Figs. 5(b) and 5(h)] suggests the presence of two peaks: (1) one at ~ 531 eV, likely from WO_3 and (2) an additional oxygen peak at 532.1 eV. Upon annealing in O_2 for 1 h at 600 °C, the latter peak was found to shift to a higher binding energy of ~ 532.5 eV [Figs. 5(e) and 5(k)].

Silicon core level spectra for the as-deposited films [Figs. 5(c) and 5(i)] indicated the presence of a $\text{Si}2p$ doublet at ~ 102.9 eV. This peak along with the O1s peak at 532.1 eV indicates a sub-stoichiometric oxide (SiO_x , $x < 2$).⁴⁹ After the anneals, the $\text{Si}2p$

doublet was shifted to ~ 103.2 eV and increased in magnitude. This shift in the $\text{Si}2p$ doublet along with the shift in O1s to 532.5 eV indicates the formation of stoichiometric SiO_2 .

Table II lists the atomic percentages of elements surveyed (W, O, Si, C, and N). The ratio of tungsten to silicon + tungsten [$\text{W}/(\text{Si} + \text{W})$] was found to be 0.45 for films deposited at 203 °C, but 0.53 for films deposited at 328 °C, suggesting a relative increase in the WO_3 content at 328 °C. The 328 °C films also had a lower overall impurity content with lower concentration of carbon consistent with the lower GPC, reduced onset temperature for crystallization, and higher density.

After annealing at 600 °C in O_2 , the concentration of carbon was found to be reduced in films deposited at 203 °C films but unchanged within error for the 328 °C films. Interestingly, the $\text{W}/(\text{Si} + \text{W})$ ratio was found to decrease for all films post-anneal. The reason for this is discussed in Sec. III D 2.

2. XRR

Given the surface sensitive nature of XPS, and to further analyze the morphological properties of the entire film, XRR was also performed after each isochronal annealing step. The raw XRR scans (shown in Fig. S5 in the supplementary material)²⁶ showed an interference of two or more oscillations in the XRR intensity versus 2θ data that is consistent with a film of at least two layers with different densities.²⁶ In addition, the $T_{\text{DEP}} = 328$ °C film annealed at 600 °C exhibited a subtle double hump in the critical angle, indicative of a low density layer on top of a higher density layer. It was found that a number of higher density $\text{WO}_x\text{-SiO}_y$ layers on top of a low density SiO_2 interfacial layer were needed to extract the total thickness, RMS roughness, and density from each raw scan (see Table SII in the supplementary material).²⁶ Two $\text{WO}_x\text{-SiO}_y$ layers were sufficient to model XRR scans for films as-deposited and annealed at 328 °C. However, up to two additional layers of $\text{WO}_x\text{-SiO}_y$ were needed to model the more pronounced interference seen for films annealed at 500 °C and above for $T_{\text{DEP}} = 203$ and 328 °C, respectively. Plots of XRR determined density versus thickness for 300 cycle films deposited at 203 and 328 °C are shown in Figs. 6(a) and 6(b), respectively. The total film thickness was found to decrease significantly upon annealing at 600 °C. Comparing the as-deposited films, it is seen that the 203 °C films are thicker and of lower density than the 328 °C films (22 vs 13 nm and 4.7 vs 5.6 g/cm³, respectively). Annealing at 600 °C decreased the overall thickness of both the 203 and 328 °C films (by approximately 21% and 31%, respectively). For both 203 and 328 °C, film density remained relatively constant for the thickest modeled $\text{WO}_x\text{-SiO}_y$ layer after 600 °C annealing (at ~ 4.7 and 5.5 g/cm³, respectively), while the thickness of this layer was found to decrease (from 21 to ~ 14 nm and from 12 to ~ 5 nm, respectively). This significant decrease in the thickness of the thickest modeled $\text{WO}_x\text{-SiO}_y$ layer after 600 °C annealing with little accompanying change in density may be explained by the sublimation of WO_3 , which has been reported to start at around 550 °C in the presence of water vapor.^{51,52} During annealing, trace amounts of water vapor can emanate from hydroxyls in our films and thereby enhance the volatility of WO_3 . Evidence in support of WO_3 sublimation after 600 °C annealing can also be seen in the decrease in

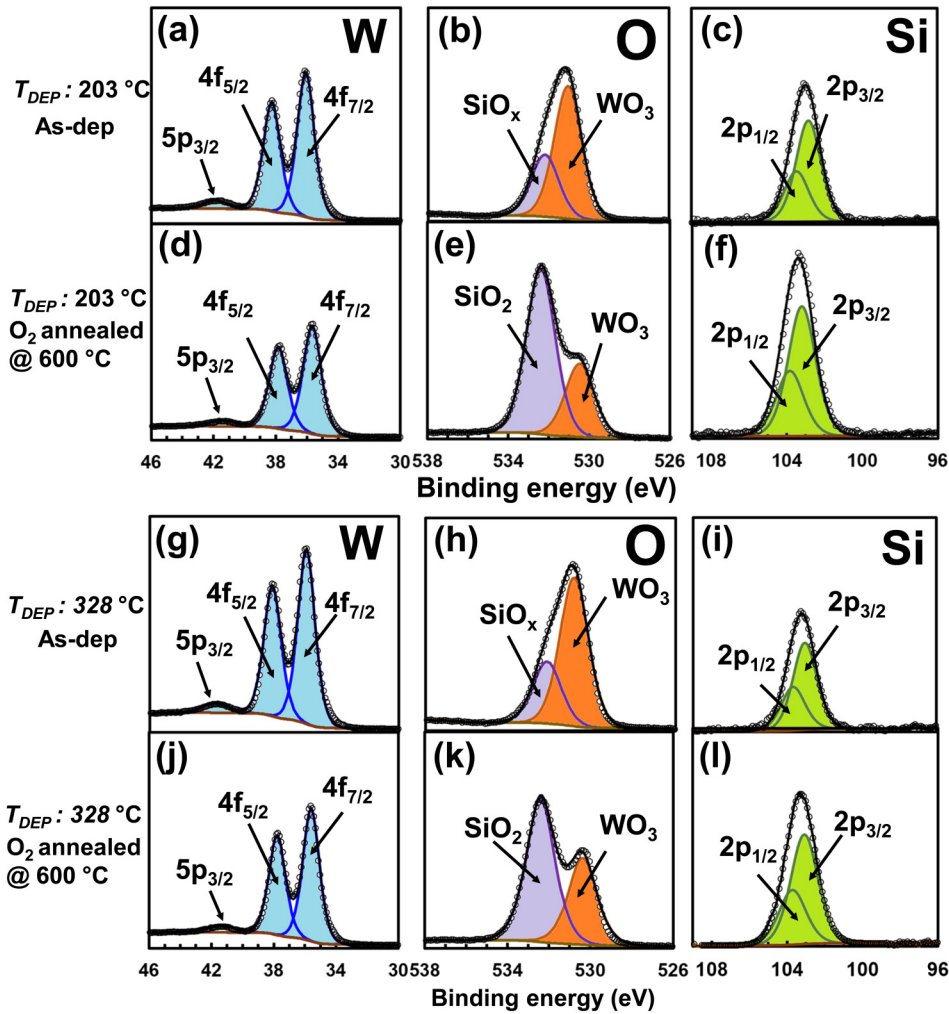


FIG. 5. XPS spectra of W4f, O1s, Si2p core levels for $T_{DEP} = 203\text{ }^{\circ}\text{C}$ ALD films [(a)–(c)] as-deposited and [(d)–(f)] 600 $^{\circ}\text{C}$ in O_2 ; and $T_{DEP} = 328\text{ }^{\circ}\text{C}$ ALD films [(g)–(i)] as-deposited and [(j)–(l)] annealed at 600 $^{\circ}\text{C}$ in O_2 .

TABLE II. Comparison of atomic (%) from the XPS quantification of as-deposited and annealed films. Uncertainty in quantitation is approximately $\pm 1\%$ for tungsten and silicon, approximately $\pm 3\%$ for oxygen, and $\pm 5\%$ for carbon. Nitrogen is below the detection limit for useful quantitation.⁵⁰

Atomic (%)	$T_{DEP} = 203\text{ }^{\circ}\text{C}$		$T_{DEP} = 328\text{ }^{\circ}\text{C}$	
	As-dep	O_2 annealed	As-dep	O_2 annealed
W	16.2	12.4	21.0	14.0
O	55.3	58.8	59.2	58.6
Si	20.1	26.8	18.5	23.0
C	7.8	2.0	1.1	4.1
N	0.5	0.1	0.2	0.3
W/(Si + W)	0.45 ± 0.02	0.32 ± 0.02	0.53 ± 0.02	0.38 ± 0.02

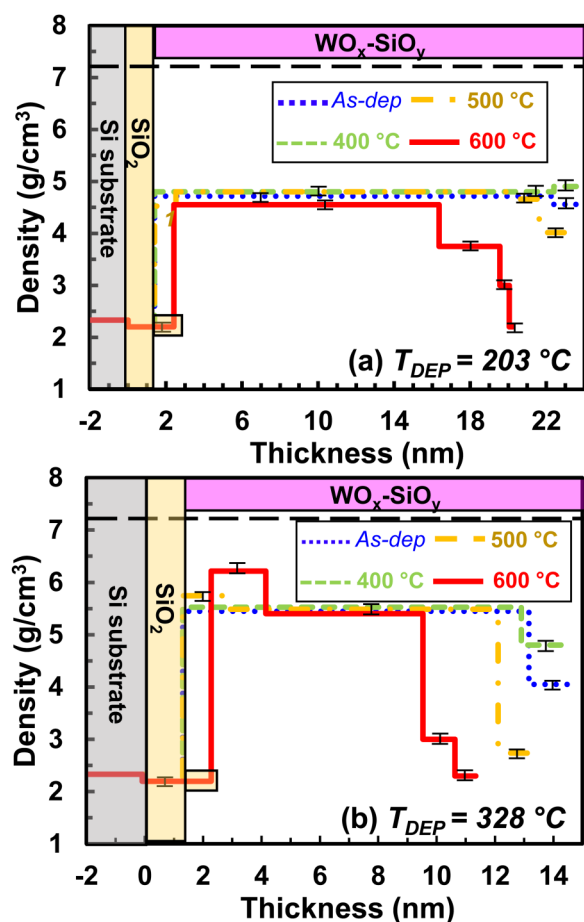


FIG. 6. Modeled XRR film density vs thickness for as-deposited (dotted line) and 400 °C (dashed line), 500 °C (dot-dashed line), and 600 °C annealed (solid line) films, for T_{DEP} = (a) 203 and (b) 328 °C. Dashed black line indicates the bulk density of triclinic WO_3 (Ref. 39). Error bars indicate the range of densities where the goodness of fit (χ^2) remains constant.

the density of the modeled WO_x-SiO_y layer at the surface: from 4.6 to 2.2 g/cm³ and 4.1 to 2.3 g/cm³ for T_{DEP} = 203 and 328 °C, respectively. The sublimation of WO_3 would leave the surface rich in SiO_2 and potentially porous indicated by the large surface RMS roughness compared to the low density film thickness (~ 0.4 to <1 nm for T_{DEP} = 203 and 328 °C). This also explains the decrease in the W/(Si + W) at. % ratio seen in XPS after 600 °C annealing (Table II).

Finally, XRR modeling suggested a slight increase in the thickness of the SiO_2 layer adjacent to the substrate (from ~ 1.3 to 2.4 nm) after 600 °C annealing for both T_{DEP} = 203 and 328 °C, likely resulting from the oxidation of the underlying silicon substrate. Additionally, a thin layer of higher density WO_x-SiO_y (5.7 and 6.2 g/cm³) just above the SiO_2 layer was needed to model the T_{DEP} = 328 °C films following 500 and 600 °C annealing, likely due

to the onset of crystallization at 500 °C (see Fig. 4). The thickness of this high density layer is consistent with the XRD Scherrer calculation of average crystallite size (see Table SI in the supplementary material).²⁶

3. Residual gas analysis

As a heteroleptic precursor with two types of reactive ligands (*t*-butylimido and trimethylsilylmethyl), BITSW can experience competition between its ligands when undergoing a surface chemical reaction where one ligand may react preferentially over the other depending on the temperature of the substrate. To shed some light on potential reaction mechanisms involved during the BITSW/ O_2 plasma ALD process, partial pressures of *t*-butylamine (TBA), tetramethylsilane (TMS), NO, and NO_2 were measured simultaneously using an *in situ* RGA. TBA and TMS are the expected ligand exchange reaction by-products of the *t*-butylimido and trimethylsilylmethyl ligands of BITSW with the surface hydroxyl groups of the substrate. Three potential surface reactions are illustrated in Fig. 7.

A pulse sequence of 6/60/60/20 s BITSW/ N_2 / O_2 plasma/ N_2 was used to ensure the saturation of both precursor and oxidizing reactions as well as provide sufficient time for simultaneous multi-channel sampling by the RGA. RGA results for the first nine cycles at deposition temperatures of (a) 203 and (b) 328 °C are plotted in Fig. 8. Starting with the initial BITSW pulse on fresh native SiO_2/Si substrates, spikes were detected in the concentration of both TBA and TMS at both 203 and 328 °C. At both deposition temperatures, the TBA spike was significantly larger than the TMS spike, suggesting that in addition to the expected exchange through the highly reactive trimethylsilylmethyl ligand,² BITSW also nucleates through the exchange of *t*-butylimido ligands with the surface -OH groups. Since both TBA and TMS have relatively high vapor pressures even at room temperature,⁵³ there should be little to no condensation losses at the RGA, suggesting that relative concentrations detected reflect the reactions occurring on the wafer. The subsequent N_2 purge drops both TBA and TMS concentrations to their respective baseline values.

During the O_2 plasma pulse, there is a marked increase in the concentrations of NO_2 and NO, an indication that the *t*-butylimido ligands attached to the surface were oxidized into these gaseous by-products. The following N_2 purge drops both NO_2 and NO partial pressures (as well as that of the TBA) to their respective baseline values. The additional spike in TBA seen at the beginning of the O_2 plasma pulse is not detected at shorter BITSW pulse durations (see Fig. S6 in the supplementary material)²⁶ and, therefore, detection at longer BITSW pulse times may be due to the reaction of O_2 plasma with residual downstream BITSW condensate built up at a cold spot in the system during the longer BITSW pulses.

Examining subsequent ALD cycles, it is seen that at T_{DEP} = 203 °C, the TBA concentration spike during the BITSW pulse settled to a steady state peak pressure of $\sim 3 \times 10^{-7}$ Torr after the first three cycles, while the peak concentration of the TMS spikes decayed to near the baseline pressure of 2×10^{-8} Torr and, thereafter, remained around this value. This behavior can be attributed to a slight change in ligand selection due to the changing

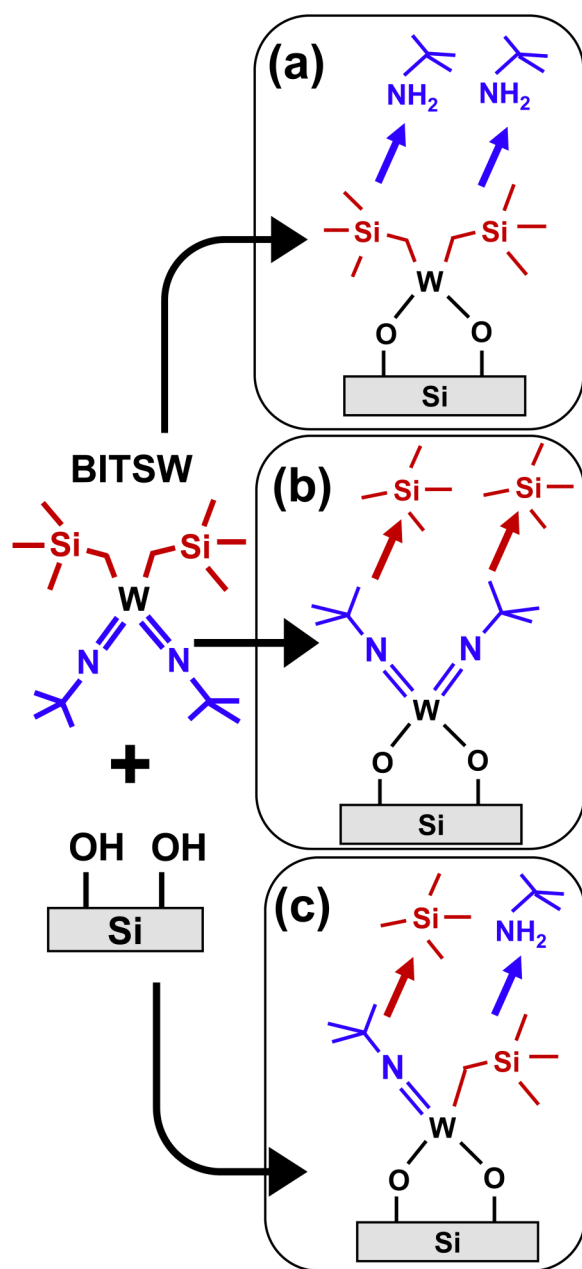


FIG. 7. Schematic illustration of three possible nucleation scenarios of BITSW with surface hydroxyl groups and their respective by-products via (a) *t*-butylimido ligands, (b) trimethylsilylmethyl ligands, and (c) a mix of *t*-butylimido and trimethylsilylmethyl ligands.

surface, from -OH terminated groups on silicon during the first few ALD cycles to -OH terminated groups on a WO₃ layer that results after three ALD cycles. A similar settling of TBA and TMS peaks back to steady state concentrations occurred by the second

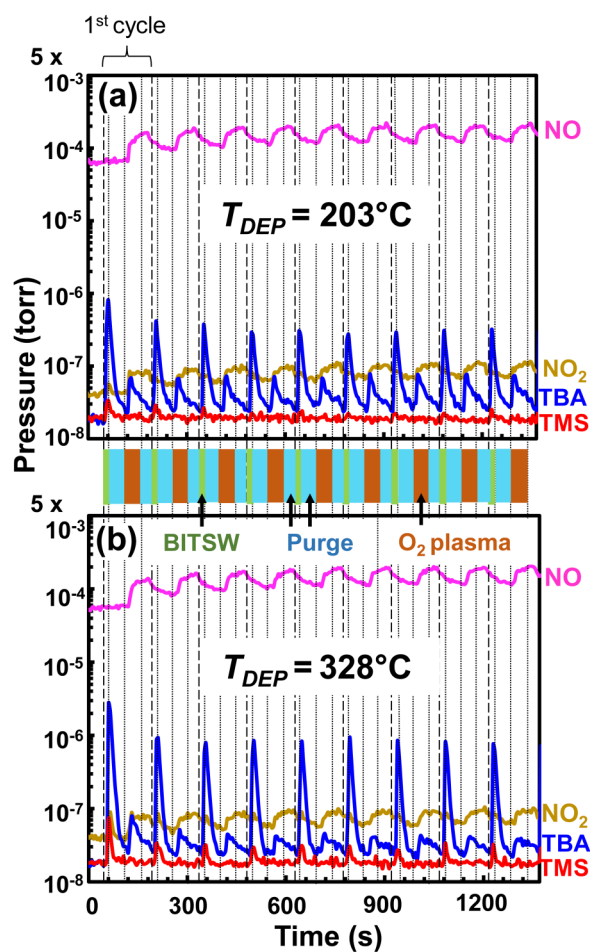


FIG. 8. Concentration of TMS, TBA, NO₂, and NO reaction by-products plotted vs time over nine ALD cycles for (a) $T_{DEP} = 203^{\circ}\text{C}$ and (b) $T_{DEP} = 328^{\circ}\text{C}$. ALD half-cycle pulses of BITSW (green block) and O₂ plasma (orange block) are interspersed with N₂ purges (blue blocks) with dashed/dotted lines to aid the eye.

cycle at $T_{DEP} = 328^{\circ}\text{C}$. Likewise, the magnitudes of the NO and NO₂ concentration spikes during the O₃ pulses also settled to steady state peak values during the same number of the respective cycles at each T_{DEP} .

The observation that both TBA and TMS peak spikes settle to a steady state within the first few cycles at both deposition temperatures is consistent with little to no nucleation delay and/or rapid closure of the film [Fig. 2(a)]. The more rapid settling of reaction products to steady state values at 328 °C suggests that nucleation and surface conversion are more rapid than at 203 °C. The complete elimination of the TMS spike after three cycles at $T_{DEP} = 203^{\circ}\text{C}$ indicated little to no competition between the *t*-butylimido and trimethylsilylmethyl ligands after the first few cycles, so that subsequent growth likely took place almost entirely through the *t*-butylimido ligands. At the higher $T_{DEP} = 328^{\circ}\text{C}$; however, there is

a clear, albeit small, component of steady state growth that occurred through the trimethylsilylmethyl ligand, as indicated by the continued presence of the TMS peak in subsequent cycles. This explains the lower $W/(Si+W)$ at.% ratio seen for films as-deposited at 203 °C when compared to 328 °C (Table II).

The specific ligands involved influence the growth rate, composition, and film properties. For example, when nucleation and growth take place through *t*-butylimido ligands, more trimethylsilylmethyl groups are left behind on the surface than *t*-butylimido ligands [as illustrated in Fig. 7(a)]. The subsequent O_2 plasma exposure oxidizes these remaining groups, leaving behind SiO_x (in addition to WO_3) and potentially carbon,^{54,55} as *t*-butylimido ligands left behind likely decompose to a volatile isobutene by-product via β -hydrogen elimination.⁵⁶ At 203 °C, the domination of the surface reaction via the *t*-butylimido ligand(s) likely contributed to a higher growth rate and a lower film density because the remaining trimethylsilylmethyl ligands may incorporate into the growing film during the O_2 plasma exposure. This is evidenced by the higher content of Si and C in the 203 °C film (see Figs. 2 and 4, and Table II). At $T_{DEP} = 328$ °C, greater participation of the trimethylsilylmethyl ligand(s) in the surface reaction [evidenced by the higher TMS RGA peak as in Fig. 7(c)] resulted in reduced Si and C incorporation. Combined with the higher TBA peaks, indicating higher overall release of *t*-butylimido ligands, this contributed to a lower GPC and a higher film density for the 328 °C film (see again Figs. 2 and 4, and Table II).

E. Thermal ALD using H_2O

Finally, thermal ALD was attempted at $T_{DEP} = 203$ and 308 °C using H_2O as the oxygen source. However, 300 cycles of a pulse sequence of 2/15/60/30 yielded little to no WO_x-SiO_y films (see Fig. S7 in the supplementary material).²⁶ Inhibiting behavior toward film growth using H_2O as the oxygen source was reported for SnO (Ref. 55) and lithium silicate films,⁵⁷ in which it was suggested that the inhibition of growth was due to the formation of a hydrophobic, siloxane ligand network on the surface. The absence of film growth here using H_2O as the co-reactant could, thus, hypothetically be inhibited due to a similar process. However, further work would be required to confirm.

IV. SUMMARY AND CONCLUSIONS

A PEALD process was developed using a novel, high stability, liquid tungsten precursor bis(*t*-butylimido)bis(trimethylsilylmethyl)tungsten and remote O_2 plasma to deposit WO_x-SiO_y composite films for the first time. Deposition was investigated over a wide temperature range of 120–370 °C, with self-limiting growth demonstrated between 203 and 328 °C. Films were investigated using XRD, XPS, spectroscopic ellipsometry, and XRR, and the ALD process was studied using *in situ* RGA. As-deposited films were found to be an amorphous mixture of WO_3 and substoichiometric SiO_x with the incorporation of carbon at 203 °C. As growth temperature was increased from 203 to 328 °C, the GPC decreased from 0.75 to 0.4 Å/cycle, accompanied by an increase in the refractive index and the density (from 1.73 to 1.96 and 4.63 to 5.6 g/cm³, respectively), a reduction in the T_{auc} optical bandgap from 3.45 to 3.27 eV, and a reduction in the C impurity content. Composition

was controlled from $W/(Si+W) = 0.45$ –0.53 over this temperature window. Post-deposition annealing in O_2 resulted in crystallization into triclinic WO_3 at 500 and 600 °C for samples deposited at 328 and 203 °C, respectively. Annealing was also found to reduce the thickness, overall density, and $W/(Si+W)$ ratio, resulting likely from the sublimation of WO_3 near the surface of the film. Thermal ALD was also investigated using H_2O as the co-reactant, but little to no film was deposited.

An RGA study of reaction by-products revealed a competition for chemisorption between the *t*-butylimido and trimethylsilylmethyl ligands in which the proportion of chemisorption via the trimethylsilylmethyl group was found to increase with T_{DEP} . The temperature-dependent ligand competition may be utilized to synthesize other films containing tungsten and silicon for various applications. For example, tungsten-silicon-nitride (WSi_xN_y), an emerging diffusion barrier material, can be synthesized using a reducing H_2 plasma co-reactant, similar to that reported by Hong *et al.*⁵⁸

In conclusion, we report the first ALD process for WO_x-SiO_y using a novel heteronuclear and heteroleptic precursor. Composition can be roughly controlled using the deposition temperature. These films should be useful for applications in catalysis, gas-sensing, and mirror coatings where high conformality and film uniformity over large areas is desired.

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AUTHOR DECLARATIONS

Conflicts of Interest

The authors have no conflicts to disclose.

Author Contributions

Kamesh Mullapudi: Conceptualization (lead); Data curation (lead); Formal analysis (equal); Investigation (lead); Methodology (equal); Project administration (equal); Software (equal); Supervision (lead); Validation (equal); Visualization (equal); Writing – original draft (lead); Writing – review & editing (equal). **Konner E. K. Holden:** Data curation (supporting); Formal analysis (supporting); Investigation (supporting); Methodology (supporting); Project administration (supporting); Resources (supporting); Supervision (supporting); Validation (supporting); Visualization (supporting); Writing – review & editing (supporting). **Jessica L. Peterson:** Investigation (supporting); Methodology (equal); Resources (equal); Validation (supporting). **Charles L. Dezelah:** Formal

analysis (equal); Project administration (equal); Resources (equal); Supervision (equal); Validation (equal); Writing – original draft (supporting); Writing – review & editing (equal). **Daniel F. Moser:** Funding acquisition (equal); Project administration (equal); Resources (equal); Validation (supporting). **Ravindra K. Kanjolia:** Funding acquisition (supporting); Project administration (supporting); Resources (equal); Writing – review & editing (supporting). **Douglas J. Tweet:** Data curation (equal); Formal analysis (equal); Methodology (equal); Supervision (equal); Validation (equal); Writing – review & editing (supporting). **John F. Conley, Jr.:** Conceptualization (equal); Data curation (equal); Funding acquisition (lead); Project administration (lead); Resources (lead); Supervision (lead); Validation (equal); Visualization (equal); Writing – review & editing (equal).

DATA AVAILABILITY

The data that support the findings of this study are available within the article and its supplementary material (Ref. 26).

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