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Pulsed-N_2 assisted growth of 5-20 nm thick β-W films

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A technique to deposit 5-20 nm thick β-phase W using a 2-second periodic pulse of 1 sccm-N_2 gas on Si(001) and SiN(5 nm)/Si(001) substrates is reported. Resistivity, X-ray photoelectron spectroscopy and X-ray reflectivity were utilized to determine phase, bonding and thickness, respectively. X-ray diffraction patterns were utilized to determine the crystal structure, lattice constant and crystal size using the LeBail method. The flow rate of Nitrogen gas (continuous vs. pulsing) had significant impact upon the crystallinity and formation of β-phase W. [http://dx.doi.org/10.1063/1.4935372]

I. INTRODUCTION

Thin β phase W films exhibit a giant spin Hall effect which can be integrated into a non-volatile spin logic device to interact with an adjacent magnetic layer.[1,2] Tungsten films thicker than 5 nm naturally transform to bulk α phase, making it challenging to produce β-W thick enough for device fabrication under large scale manufacturing conditions.[3,4] For example, the W film must be thick enough to survive the etch of the magnetic films and be under the spin diffusion length for effective device functioning which puts the desirable thickness in the 10-20 nm range.[5] Introducing O_2 during the deposition has been shown to stabilize β tungsten enabling the growth of thicker films, but high concentrations of it forms an amorphous-like phase.[6–12] In addition, it may be undesirable to introduce O_2 into deposition chamber which also grows ferromagnetic metals.

Introducing N_2 gas during deposition is a natural alternative to O_2, however it forms tungsten-nitride crystals or an amorphous-like phase but not a β-phase.[8,10,13] It appears that N_2 drastically inhibits the grain growth (similar to high concentrations of O_2), which is undesirable.[11] This creates a need to form 10-20 nm thick β-W films without the assistance of O_2 gas flow and find the optimum conditions for N_2 flow during tungsten deposition.

In this article, β phase W films of thicknesses up to 20 nm have been fabricated using a 2 second periodic 1 sccm N_2 pulse. The growth kinetics are altered by changing the N_2 gas concentration in the chamber during the deposition which enables the deposition of up to 20 nm thick β-W. The crystal size of these films are ~5 nm and resistivities are ~160 $\mu\Omega$ cm, which show promise to be introduced into a fabrication facility to grow β-W for large scale device fabrication.

II. EXPERIMENTAL

Two substrates: single crystal Si(001), and 5 nm of SiN on Si(001) were chosen to deposit the W films. Four different thicknesses of W were deposited: 5, 7.5, 10, and 20 nm. Six 5 nm thick W films were grown, three on each substrate. Three films grown on the Si substrate with the three following different N_2 gas conditions: 1 sccm, 2 sccm, and a 2 second periodic-1 sccm pulse. Three

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TABLE I. W films deposited under different substrates and process conditions.

Thickness (nm) (From XRR)	N_2 gas flow	5 SiN	Resistivity ($\mu\Omega$ cm)	Crystal size (nm)	Lattice constant (^{o}A)	Dominant phase
5(4.8)	1 sccm	No	135.9	1.6	-	Amorphous-like
5(4.5)	2 sccm	No	168.9	1.1	-	Amorphous-like
5(4.9)	2s-1-sccm pulse	No	135.9	2.3	5.04	β
5(4.9)	1 sccm	Yes	185.8	1.8	-	Amorphous-like
5(4.7)	2 sccm	Yes	189.1	1.1	-	Amorphous-like
5(4.7)	No	Yes	158.3	2.8	5.04	β
7.5(7.3)	No	Yes	24.9	7.9	3.15	α
7.5(7.1)	1 sccm	Yes	172.7	2.3	4.9	β
7.5(7.7)	2s-1-sccm pulse	Yes	176.5	4.7	5.00	β
7.5(7.2)	No	No	24.3	8.3	3.15	α
7.5(7.1)	1 sccm	No	166.55	2.2	5.04	β
7.5(7.7)	2s-1-sccm pulse	No	153.6	3.9	5.03	β
10(9.9)	No	Yes	23.7	10.2	3.14	α
10(10.5)	2s-1-sccm pulse	Yes	174.6	5	5.30	β
10(9.7)	No	No	20.9	10.4	3.14	α
10(10.4)	2s-1-sccm pulse	No	159.7	4.9	5.00	β
20(21)	2s-1-sccm pulse	Yes	163.3	7.8	5.00	β
20(21)	2s-1-sccm pulse	No	149.49	7.0	5.01	β

5 nm thick films were grown on the SiN(5 nm)/Si(001) substrate using the following three N_2 gas conditions: 1 sccm, 2 sccm and no N_2 during the deposition.

Six 7.5 nm thick W films were grown on both substrates under the following three different N_2 gas conditions: 2 second periodic-1-sccm pulse, 1 sccm continuous flow and no N_2 during the deposition.

Four 10 nm thick films were grown on the two different substrates with two different flow conditions: 2 second periodic-1-sccm pulse and without N_2. Two 20 nm thick films on the two substrates were grown using a 2 second periodic-1- sccm pulse of N_2 gas.

The resistivity of each film was measured using a four point probe technique with KLA Tencor's RS-100 instrument. Lattice parameters and crystal sizes were calculated from X-ray diffraction patterns using the LeBail method (Bruker TOPAS, version 4.2) to characterize the phases and estimate the lattice parameter which are displayed in Table I. A Bruker X-ray diffractometer was utilized and configured in a parallel-beam geometry with a fixed 0.5° incidence angle (sealed Cu source). Beam conditioning consisted of a graded parabolic mirror with mechanical slits on the incident beam and a parallel plate collimator for the diffracted beam. Detector (2θ) scans covered a range of 20° to 120° in 0.05° steps. Instrument function parameters were determined using NIST Standard Reference Material 1976 (α-Al_2O_3). X-ray photoelectron spectroscopy was performed to understand the chemical state of the films using Thermoscientific Theta probe. X-ray reflectivity was measured to estimate the thickness of each film with a Jordan Valley BEDE Metrix-L (BML) X-ray diffractometer was used to measure thickness. A 2.2 kW Cu sealed tube source (0.154 nm) with a beam of a few millimeters (2 mm × 2 mm) was scanned from 0 to 20000 arcseconds at a step size of 10 arcseconds for XRR measurements.

III. RESULTS

A. X-ray diffraction analysis

The X-ray diffraction patterns of 5 nm, 7.5 nm and 10 nm, 20 nm W films are displayed in Fig.1, Fig.2, Fig. 3, respectively. The four X-ray diffraction patterns of the 5 nm W films with 1 sccm and 2 sccm N_2 gas when grown on both, Si(001) and SiN(5 nm)/Si(001), substrates show amorphous-like diffraction patterns as displayed in Fig. 1. A strong crystalline diffraction is observed in the two 5 nm films grown on SiN(5 nm)/Si(001) without any N_2 gas and the 5 nm film

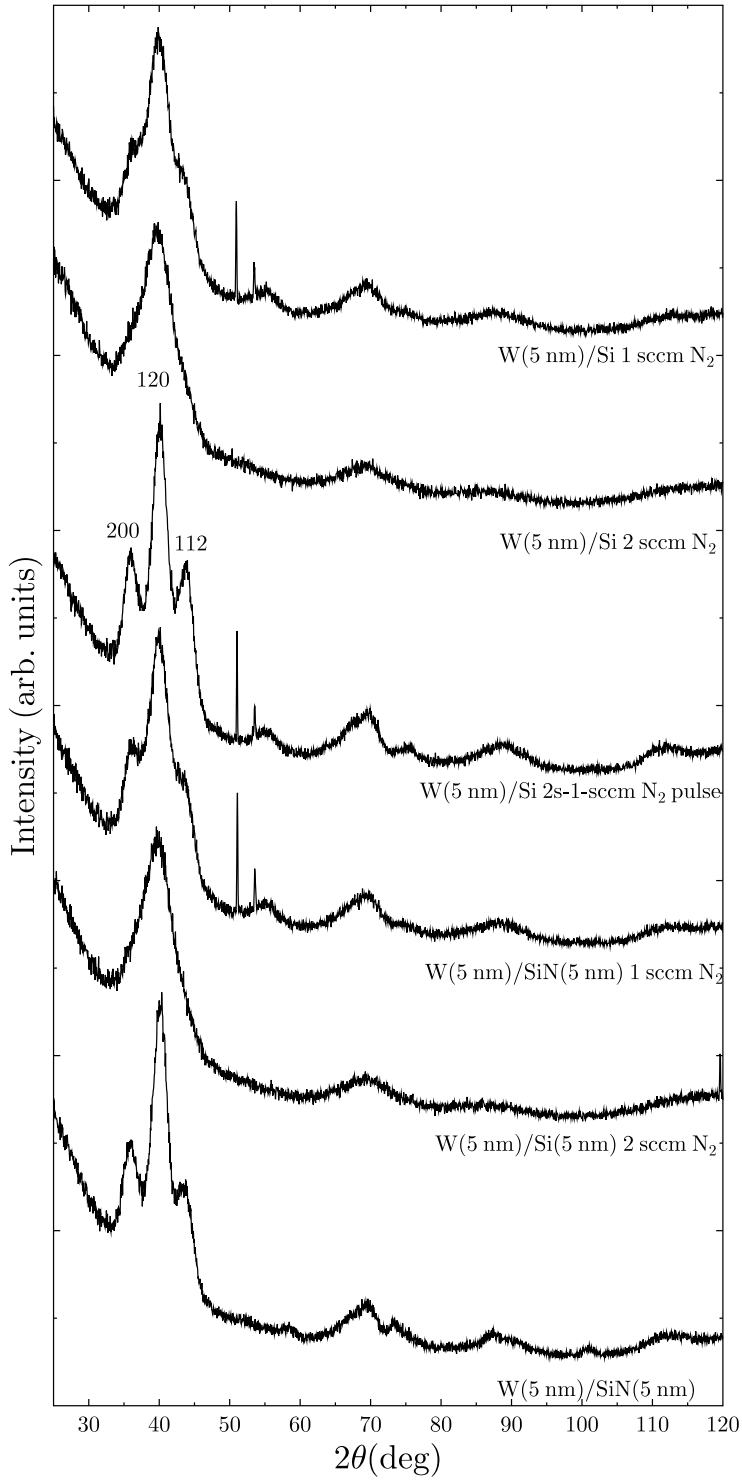

FIG. 1. X-ray diffraction patterns of the 5 nm W films deposited on the substrates as indicted.

deposited on the Si substrate with pulse N_2 gas. These have a lattice parameter of 5.04 Å when fit using LeBail method.

Two 7.5 nm W films, deposited on Si(001) and SiN(5 nm)/Si(001) substrates form an α dominated phase with lattice constant of 3.15 Å and crystallite size around 8 nm. The two 7.5 nm W films with continuous flow of 1 sccm N_2 gas on SiN(5 nm)/Si(001) and Si(001) substrates show a smaller

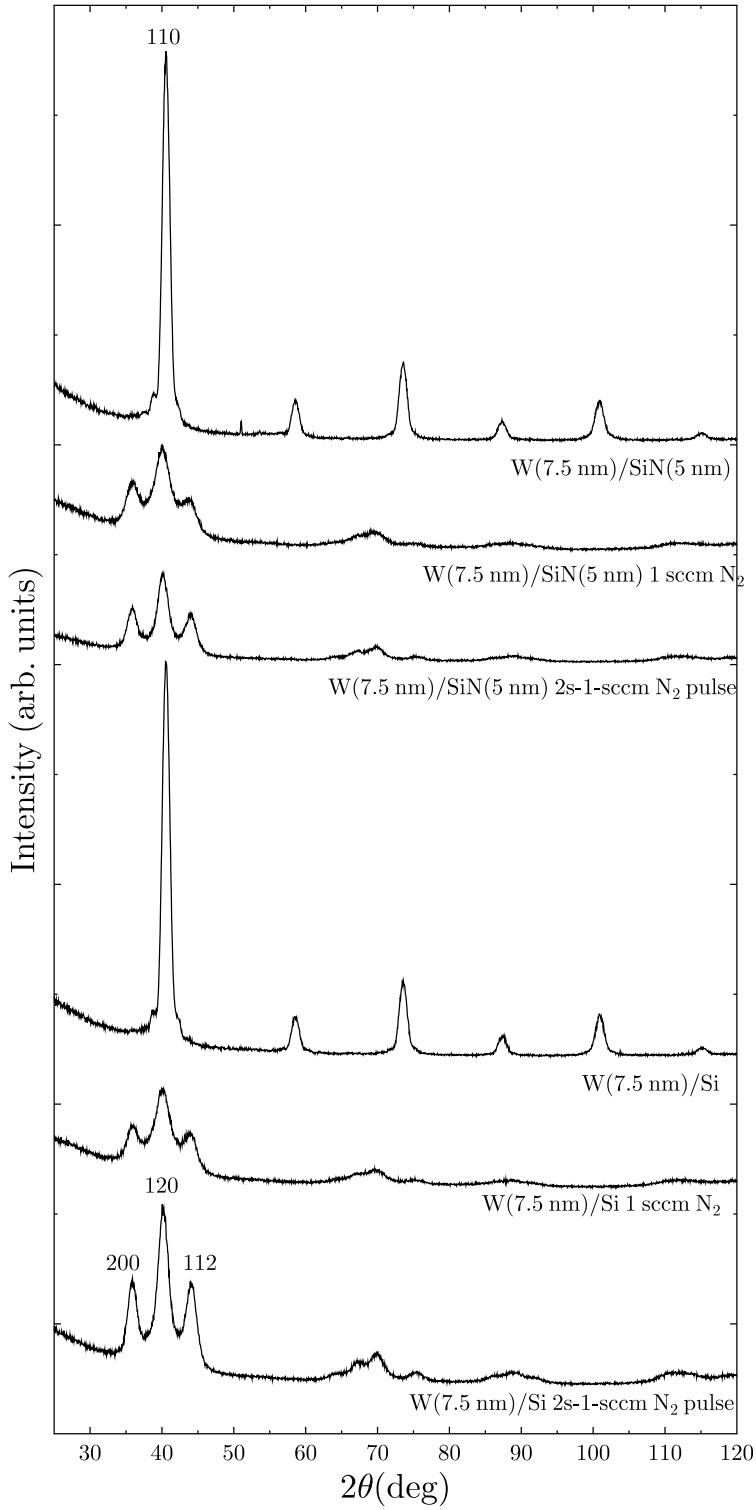

FIG. 2. X-ray diffraction patterns of the 7.5 nm W films deposited on the substrates as indicted.

crystallite size of 2.3 nm and 4.7 nm and a β dominant phase with lattice constants of 4.9 Å and 5.04 Å respectively. The smallest crystal size is seen in the two films grown with a pulsed N_2 gas condition on both substrates. Lattice constants and crystal sizes are 5.00 Å, 4.7 nm and 5.03 Å, 3.9 nm for the SiN(5 nm)/Si(001) and Si(001) substrates respectively.

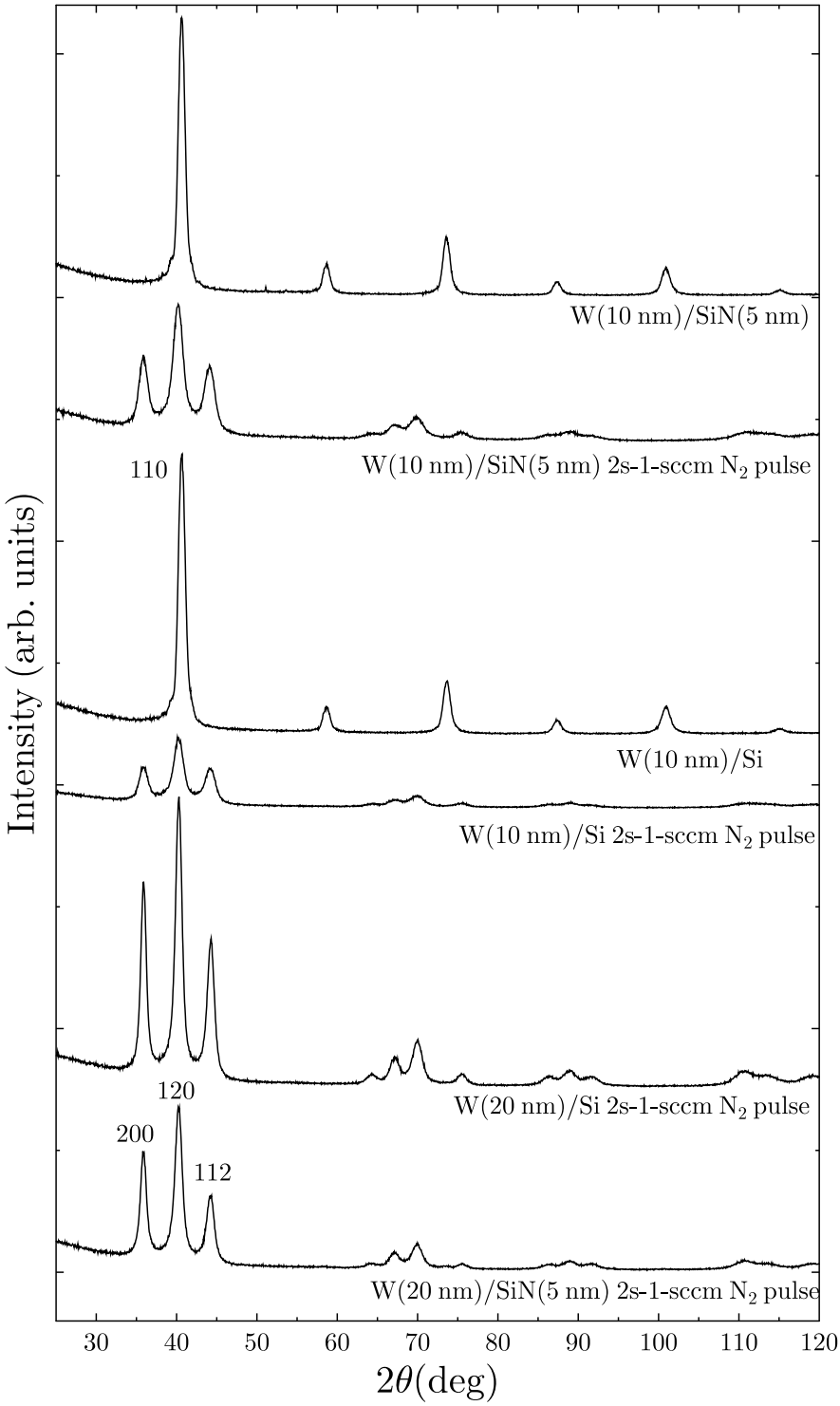

FIG. 3. X-ray diffraction patterns of the 10 nm and 20 nm W films deposited on the substrates as indicted.

The X-ray diffraction patterns for 10 nm and 20 nm films show a smaller crystal size, as seen in Fig. 3, also the β-W(200), β-W(211) peaks appear in films with 2s-1-sccm N_2 pulse samples. These films show a reduction in crystallite size in comparison to their α-W counter parts(similar thickness, Table I). Lattice parameter and crystallite size are 5.00 Å, 5.01 Å and 7.0 nm, 7.8 nm for 20 nm β-dominated W films. The 10 nm α dominated W films lattice constants and crystallite size are

3.14 Å, and 10.4 nm, 10 nm. The 10 nm β dominated films have a 5.00 Å and 5 nm lattice parameter and crystallite size, respectively.

B. X-ray photoelectron spectroscopy

The XPS results for all the films show a WO_3 peak in addition to a metallic peak of W as displayed in the Fig. 4 and Fig. 5. The 5 nm W films with different N_2 gas flow conditions on two different substrates are displayed in Fig. 4. The 5 nm W films grown on a SiN(5 nm)/Si(001) substrate with a 2 sccm of N_2 gas during the deposition cycle are displayed in Fig. 4(a). This shows significant W^{+0} peak at 30.7 eV and W^{+6} peak around 35.06 eV.[14,15] A broad suboxide peak $W^{+x}(0 < x < 6)$ was necessary to obtain a better fit at 34.1 eV. The 5 nm W film grown during a N_2

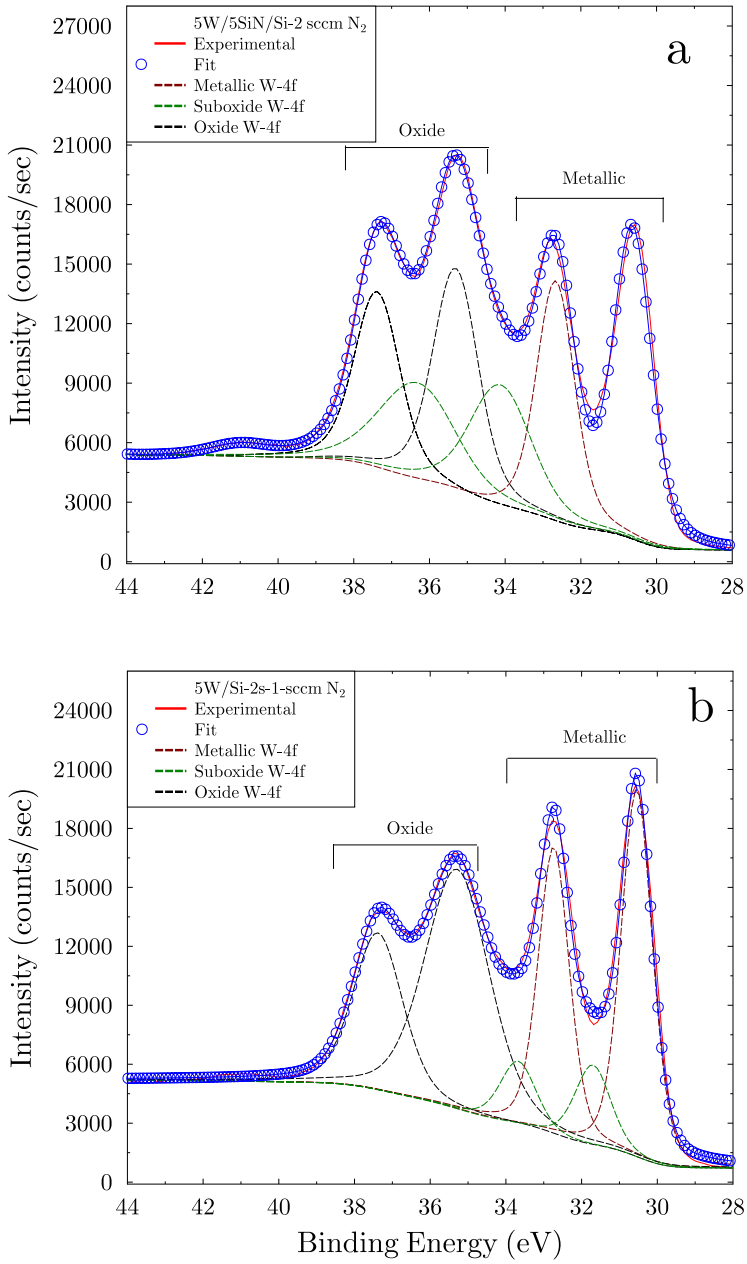

FIG. 4. a.) X-ray photoelectron spectroscopy result of 5 nm amorphous-like W film. b.) X-ray photoelectron spectroscopy result of 5 nm βW film.

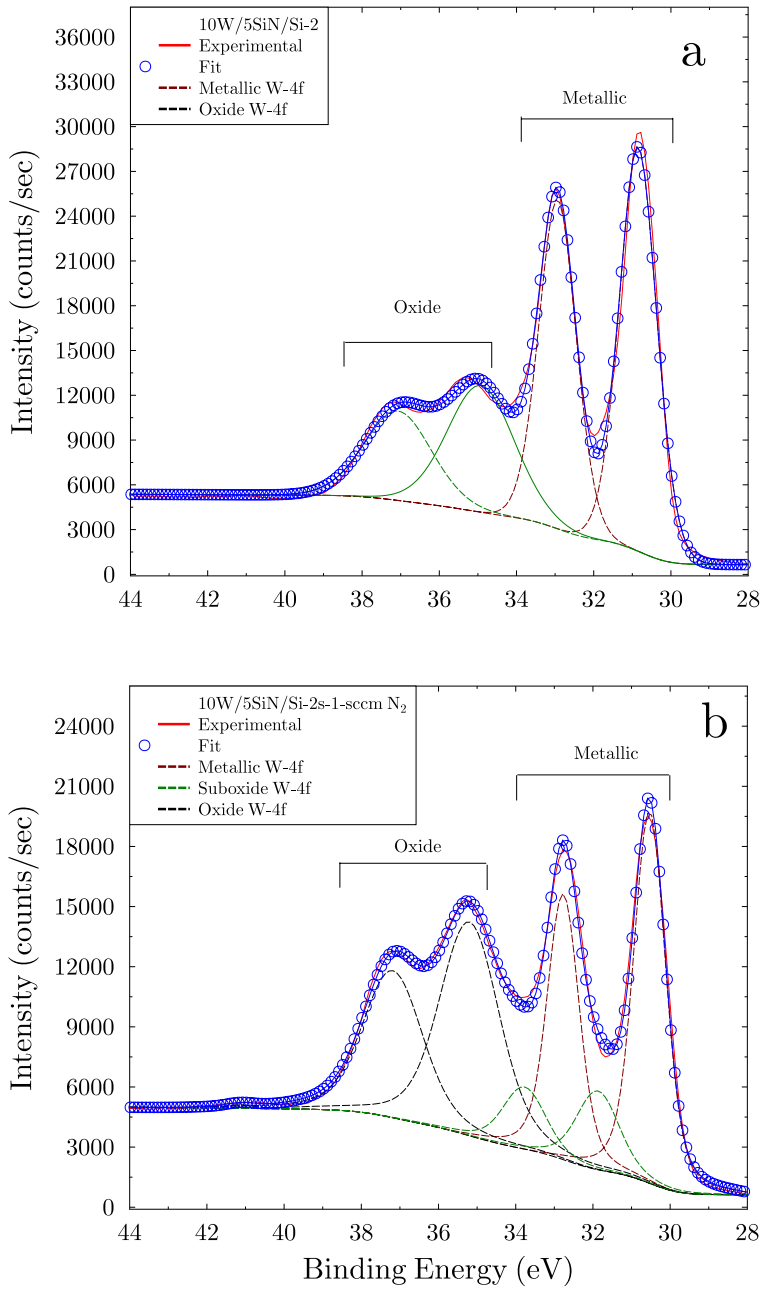

FIG. 5. a.) X-ray photoelectron spectroscopy result of 10 nm α W film. b.) X-ray photoelectron spectroscopy result of 10 nm βW film.

pulse was used during the deposition, as displayed in Fig. 4(b). This resulted in a increase in W^{+0} peak at 30.6 eV and W^{+6} peak around 35.3 eV with a suboxide of $W^{+x}(0 < x < 6)$ at 31.7 eV. A similar spectrum was observed for the rest of the 5 nm films with both metallic and oxide character of W in all the films.

The W film grown on a SiN(5 nm)/Si(001) substrate with W^{+0} peak at 30.9 eV and W^{+6} peak around 34.9 eV as displayed Fig. 5(a). No suboxide peak was necessary to obtain a better fit for this film. The 10 nm W film deposited during a N_2 pulse was used during the growth on a SiN(5 nm)/Si(001) substrate as displayed in Fig. 5(b). This resulted in W^{+0} peak at 30.5 eV and W^{+6} peak around 35.2 eV with a suboxide of $W^{+x}(0 < x < 6)$ at 31.9 eV was added to improve the fit. Similar spectrums were observed for the 7.5 nm and 20 nm films.

IV. DISCUSSION

The lattice constants of the β-phase W films are in agreement with previous β phase films grown with and without O_2.[15–19] However, the films are less resistive than previous β-W films which are typically around ~200 $\mu\Omega$ cm, which maybe beneficial for producing devices with lower resistances than films grown with O_2.[5,6] The α phase-W films have two peaks around W(110) these peaks were not commented for in earlier studies and fit well with a W_5Si_3. In addition, the β W(210) and α W(110) peaks are very close to each other which cannot be resolved using the Lebail method which does not take the site occupancy into account. However, the average grain size decreases whenever the β W(200) and (211) peaks appear around the β W(210)/α W(110). This characteristic smaller grain size is another indication of the formation of a β phase.

Depositing a 5 nm W film on SiN without any N_2 gas forms a β phase film. However depositing 5 nm on bare Si forms an α phase. This is similar to our previous findings where 5 nm of W deposited on SiO_2 forms a β phase, which was attributed to the uptake of O_2 causing the formation of β-W.[5] However the SiN substrate does not provide the oxygen and the roughness of the substrate and the thickness (5 nm) of W film constrain the average grain size to be around 2.8 nm, thus restricting the film to be in β phase. The Si substrate does not offer such a surface roughness, or source of oxygen, and the film readily forms an α phase.

A continuous N_2 gas flow renders the 5 nm thick W amorphous-like on both substrates similar to previous findings.[8,10,13] However, when a N_2 pulse is introduced, the concentration is sufficient to kinetically constrain the grain growth to form β W. The XPS results of these films shows metallic character present in the all the W films. The native oxide peak of β-W is higher than the α-W of similar thickness. This can be interpreted as higher oxygen gettering capacity of β-W. The metallic peak of β-W is higher than amorphous-like W film of similar thickness and is attributed to the increased crystallinity in the β-W than the amorphous films.

As the thickness is increased to 7.5 nm and 10 nm there are more W atoms to nucleate and grain size increases to form thermodynamically stable α phase on Si and SiN substrates when no N_2 is introduced. When a continuous 1 sccm of N_2 gas is flown during deposition for the 7.5 nm W film on both substrates the film forms a β phase W but with a reduced grain size. However, a N_2 pulse during the 7.5 nm growth yielded much sharper β- phase diffraction pattern with a larger grain size similar to the 5 nm thick film. For 10 nm and 20 nm thick W films on both Si(001) and SiN substrate only pulsing the N_2 resulted in β-W with larger average grain size and sharp diffraction patterns, indicating a high quality β-W film.

These findings demonstrate the importance of pulsing the N_2 to achieve β. When inert impurities such as N_2 are introduced into the deposition chamber, they interfere with the nucleation and grain growth of the deposited film. These impurities can either act as a roadblock to grain growth or act as a nucleation site resulting in smaller grain sizes. However if large concentrations of N_2 gas are introduced, about 1 or 2 sccm, it blocks W-metal from forming a crystalline phase and an amorphous-like film is formed. Upon lowering the concentration by pulsing, a kinetically grown phase which has much larger grain size is able to be produced. The 7.5 nm film still crystallizes to form a β phase in presence of 1 sccm continuous flow due to the availability of more W atoms but it has smaller grain size. The 5 nm thick W lies on the boundary of kinetic and thermodynamic stability offered by the SiN substrate or continuous N_2 gas flow. For films 10 nm and above pulsing the N_2 is required to form β-W films with larger grains.

V. CONCLUSION

In conclusion, a novel technique to deposit thick β phase films by kinetically controlling the growth by introducing a 2 second periodic pulse of 1 sccm N_2 gas from 5 to 20 nm thick films is demonstrated. The inert nature of N_2 gas will not effect other metal targets in the deposition chamber and offers a much more versatile alternative than using O_2. These less resistive β phase films should produce devices with lower resistances which maybe beneficial for improved efficiency and power consumption. It would be interesting to explore these findings on other metals that have a β-phase such as Ta.

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