

Contents lists available at ScienceDirect

Applied Surface Science



journal homepage: www.elsevier.com/locate/apsusc

Full Length Article

Highly selective atomic layer deposition of $MoSiO_x$ using inherently substrate-dependent processes

Jong Youn Choi^a, Christopher F. Ahles^a, Keith T. Wong^c, Srinivas Nemani^c, Ellie Yieh^c, Andrew C. Kummel^{b,*}

^a Materials Science and Engineering Program, University of California, San Diego, La Jolla, CA 92093, United States

^b Department of Chemistry & Biochemistry, University of California, San Diego, La Jolla, CA 92093, United States

^c Applied Materials, Inc., Santa Clara, CA 95054, United States

ARTICLEINFO	A B S T R A C T
<i>Keywords:</i> Atomic layer deposition Area-selective deposition Selective oxide deposition	A resistive MoSiO _x film was deposited with high selectivity on Si in preference to SiO ₂ and SiN using MoF ₆ , Si ₂ H ₆ and O ₂ as reactants. Two different approaches were demonstrated via thermal atomic layer deposition (ALD). First, ALD of MoSiO _x by sequential dosing of MoF ₆ , Si ₂ H ₆ and O ₂ (ABC-type) at 200 °C followed by an ex-situ post-deposition anneal (PDA) in O ₂ at 350 °C was performed. The growth of the film using the ABC-type de- position was limited to ~5.25 \pm 0.5 nm because the insulating film inhibits the MoF ₆ and Si ₂ H ₆ ALD reaction. The second method was to grow MoSi _x at 120 °C and employ a post-deposition anneal in O ₂ /He at 350 °C (AB + C-type) to form MoSiO _x . The selectivity of this process on Si versus SiO ₂ was perfect for 10 nm of de- position on Si, as there were no nuclei or particle formation observed on the SiO ₂ surface by atomic force microscopy (AFM). The high selectivity can be obtained due to the inherent inability of MoF ₆ to react SiO ₂ and SiN surfaces. Transmission electron microscopy (TEM) of a nanoscale-patterned sample demonstrated that the

1. Introduction

As metal-oxide semiconductor field effect transistors (MOSFETs) are scaled to sub-10 nm nodes with three-dimensional features, it becomes a significant challenge to enhance the feature density and quality in patterning processes. Conventional patterning processes such as photolithography and e-beam lithography rely on multiple steps of resist patterning. These processes involve a combination of deposition and lithography followed by wet and plasma etching, which might lead to imperfect alignment and low resolution issues. [1,2] Additionally, some metals such as Cu and Co are not easy to etch. [3-5] Area selective atomic layer deposition (ALD) is of great interest in multi-patterning processes since it provides conformality, spatial uniformity and selectivity. For example, in a self-aligned double patterning (SADP) process, integration of selective ALD with lithography allows patterning sub-10 nm features with better resolution and accurate positioning. In the multiple patterning processes, sharp self-aligned selective deposition is required not only to pattern the sub-10 nm features but also to reduce the need for lithography. [1,6]. As depicted in Fig. S1(a), a conformal ALD of a spacer (low-k material) around the mandrels (sacrificial layer) might simplify the self-aligned double patterning (SADP) process by depositing only on the side walls of the lithographically defined mandrel without depositing on the top and bottom layers (see Supplement, Fig. S1(b)).

highly selective MoSiO_x can be achieved and be integrated into three-dimensional nanoscale structures.

Selective ALD of oxides is challenging since strongly oxidizing coreactants can induced reactions on any surface. For example, the most commonly used oxygen sources for metal oxide deposition are H₂O, H₂O₂, O₂ plasma and ozone (O₃) which can physisorb or chemisorb onto semiconductor, insulator, and metallic surfaces initiating ALD nucleation. [7-12] One technique for selective deposition of oxides with these strong oxidants is to add passivants or plasma etching steps every cycle or every couple of cycles to prevent any nucleation leading to selectivity loss on an unwanted surface. [15-17] For example, Mameli et al. [15] demonstrated area selective atomic layer deposition of $\sim 1.5 \text{ nm}$ thick SiO₂ on GeO₂ against Al₂O₃ by a three-step deposition (ABC-type cycle) using A: acetylacetone (Hacac), B: bis(diethylamino) silane and C: O2 plasma. They reported that the gas phase Hacac inhibitor reacts only with the Al₂O₃ substrate and not with GeO₂ or SiO₂; however, the inhibitor needed to be dosed in each ALD cycle since the O₂ plasma removed the Hacac inhibitor. Single step passivation has also been reported; for example, Hashemi et al. [16] demonstrated area selective ALD of ~30 nm ZnO on SiO₂ against Cu using diethylzinc and

* Corresponding author.

E-mail address: akummel@ucsd.edu (A.C. Kummel).

https://doi.org/10.1016/j.apsusc.2019.144307

Received 24 May 2019; Received in revised form 7 September 2019; Accepted 6 October 2019

water as ALD precursors. This was accomplished with vapor phase passivation using dodecanethiol (DDT) self-assembled monolayer (SAM) followed by an ex-situ sonication to inhibit growth on Cu. The selectivity could be expanded to 100 nm by regenerating DDT SAM every 150 ALD cycles; however, regeneration of passivation layer may also necessitate another wet selective removal step for residual passivants after the deposition process is complete. [18]

To avoid using oxidants such as H_2O or O_2 plasma, there have been studies to deposit oxide thin films by employing metal alkoxides as a precursor that can supply both an oxygen and a metal atom. [13,14,19] Atanasov et al. [19] demonstrated inherent substrate-dependent growth of TiO₂ on hydroxyl terminated SiO₂ (Si-OH) against hydrogen terminated Si (Si-H) using titanium tetra-isopropoxide (TTIP) and TiCl₄. It is hypothesized that the oxidants hydroxylate H-Si surfaces and initiate nucleation on Si. This process did not use any passivant nor seeding layers; however, the nucleation delay on Si was only sufficient to deposit 2 nm TiO₂ on SiO₂.

Inherently selective ALD is a compelling process to achieve selective deposition on the nanoscale without using passivants, seeding layers, or additional plasma steps since this relies only on the reactivity of ALD precursors with different substrates. Previously, Choi et al demonstrated on selective $MoSi_x$ deposition on Si in preference to SiO₂, SiON and SiN, [20]; MoF_6 and Si_2H_6 did not react with OH-SiO₂ and NH_x -SiN due to the chemical inertness of the strong Si-O, Si-N, SiO-H and SiN-H bonds towards the ALD precursors. In contrast, MoF_6 reacted with a H-Si surface by forming Si-MoF_x bonds which enables a chain reaction with following Si_2H_6 .

In this work, an insulating molybdenum silicon oxide ($MoSiO_x$) was deposited by ALD on silicon in preference to silicon oxide and silicon nitride using MoF_6 and Si_2H_6 and O_2 using substrate-dependent selectivity. A successful conformal $MoSiO_x$ deposition on a nanoscale three-dimensional Si sidewall with about 200:1 selectivity over SiO_2 and SiN were demonstrated which could be transferred to the multipatterning process for 3-dimensional MOSFETs.

2. Experimental

Fig. 1 shows a schematic of the vacuum chamber. The selective deposition of $MoSiO_x$ was performed in a home-built reaction chamber (ALD chamber) pumped by a turbomolecular pump and a rotary pump connected in series. The chamber had an in-situ heating and sample transfer system using a pyrolytic boron nitride (PBN) heater mounted on a manipulator. The base pressure of the reaction chamber was 8.0×10^{-8} Torr. The chamber wall was set to 80 °C and dosing lines for MoF₆, Si₂H₆, N₂ and O₂ were kept at room temperature. Pneumatic valves (UHP diaphragm sealed valve, Swagelok) controlled by a computer program (Labview 8.0) were employed to precisely regulate the valve opening times in milliseconds. The processed samples were transferred into an ultra-high vacuum (UHV) chamber equipped with X-ray Photoelectron Spectroscopy (XPS) for characterization without air exposure.

P-type Si (0 0 1) (Waferworld), thermally grown SiO₂ (Waferworld), and SiON samples (Applied Materials) were used for the selective deposition of $MoSiO_x$. Note that the SiON is actually a stoichiometric



Fig. 1. Schematic of vacuum chamber. The chamber was composed of a reaction chamber (ALD chamber), sample loading chamber, and UHV chamber equipped with X-ray photoelectron spectroscopy.

Si₃N₄ after a reactive ion etching (RIE) and O₂ plasma ashing process which mimics the surface condition of a lithographically patterned sample. The samples were rinsed sequentially with acetone, methanol and HPLC-grade water followed by a wet clean in a 0.5% HF solution for 30 s to remove native oxides. After the HF clean, the samples were rinsed again with HPLC-grade water for 10 s and blow-dried with high purity N₂. The HF cleaned samples were loaded into a sample loading chamber, and the chamber was pumped down to 5.0×10^{-6} Torr before transferring the samples to the UHV chamber. The chemical compositions of the samples were investigated using XPS in the UHV chamber before and after each experiment.

MoF₆ (Synquest Laboratories, 99%), Si₂H₆ (Air Liquide, 99.99%) and O₂ (Praxair, 10% balanced in He) were used as the ALD precursors at a temperature in the range of 120–200 °C followed by an in-situ or ex-situ O₂ anneal at 300–350 °C. As previously reported, [20] MoF₆ and Si₂H₆ selectively react with Si in preference to SiO₂ and SiN_x to form MoSi_x. Two approaches were employed to incorporate oxygen into the MoSi_x using O₂ in a thermal process. The first method was to incorporate oxygen into the film during a three step ALD cycle: MoF₆ + Si₂H₆ + O₂ at 200 °C. The dose sizes of MoF₆ and Si₂H₆ were 1.2 MegaL and 2.2 MegaL (1 Lanmuir (L) = 10^{-6} Torr × 1 s exposure of a gas). O₂ (10% balanced in He) was dosed using a leak valve at 120 mTorr for 6 mins which corresponds to 4.3 MegaL of O₂. Each precursor was separated by an N₂ purge at 90 mTorr for one minute. Additionally, an ex-situ post deposition anneal (PDA) under a constant flow of 100% O₂ at 1 SLM was performed at 350 °C in an AllWin21 rapid thermal annealing system. The ex-situ O₂ anneal was performed at ~1 atm pressure for 10 mins which corresponds to 456 GigaL of O₂. The second method was to grow a MoSi_x film selectively on a Si substrate and convert the MoSi_x film into MoSiO_x at high temperature; the ALD of MoF₆ + Si₂H₆ was performed at 120 °C followed by an in-situ anneal in O₂ (10% balanced in He) at 15 Torr for 10 mins which corresponds to 900 MegaL of O₂ at 350 °C.

A monochromatic Al K α X-ray source and a hemispherical analyzer (XM 1000 MkII/SPHERA, Omicron Nanotechnology) were used for XPS. The anode voltage was set to 10 kV with a filament emission current of 25 mA. The focused beam size on the samples was 0.7–1 mm. For the XPS measurements, the samples were aligned to the detector to have a 30-degree take-off angle from the sample surface (i.e near glancing) for the surface sensitive detection. As the occasion demands, 60-degree take-off angle form the sample surface was also used for the bulk

composition. The peak areas of XPS spectra were normalized to the sum of all elements after a sensitivity correction using the Casa XPS v2.3 program. The topology of the deposited film was studied using AFM (Agilent 5500) in tapping mode. The nanoscale patterned sample was supplied from Applied Materials and cross-sectional TEM was performed before and after the selective $MoSiO_x$ deposition at Applied Materials.

3. Results and discussion

The sequential three-step reaction of MoF_6 , Si_2H_6 and O_2 on Si at 120 °C and 200 °C was investigated using an in-situ XPS. The chemical composition of the Si surface after each experiment step is shown in Fig. 2. Si and Mo are presented in two different bars in order to indicate the total amount (Si 2p and Mo 3d) together with the oxidized



Fig. 2. Elemental compositions at each deposition step of 3 step $MOSiO_x$ ALD. (a) At 120 °C, MOF_6 , Si_2H_6 and O_2 were sequentially dosed on HF cleaned Si. Mo was not fully oxidized after an ALD cycle at 120 °C. Additional dosing with 4.3 MegaL of O_2 increase the fraction of oxidized Mo. The ALD process was continued on the sample at 200 °C. The additional 4.3 MegaL of O_2 at 200 °C fully oxidized the Mo. Additional cycles of MOF_6 , Si_2H_6 and O_2 at 200 °C deposited ~2.2 nm thick $MOSiO_x$ film with fully oxidized Mo. (b) During the same doses, HF cleaned SiO_2 shows negligible amount of Mo detected on the surface.



Fig. 3. Elemental compositions and oxidation states of $MoSiO_x$ on HF cleaned Si from 3 Step ALD followed by in-situ and ex-situ O_2 post deposition anneals (PDA). (a) XPS compositions show fully oxidized Mo before and after the in-situ and ex-situ O_2 PDA. (b) Mo 3d peaks show complete oxidation of Mo after the ex-situ PDA at 350 °C. (c) Si 2p peak also shows full conversion of Si into $MoSiO_x$.

components (Si (ox) and Mo (ox)) which correspond to Si¹⁺ through Si⁴⁺ and Mo¹⁺ through Mo⁶⁺. Note that MoSiO_x should have both oxidized Si and oxidized Mo components.

Fig. 2(a) shows a cycle of MoSiO_x deposition at 120 °C on HF cleaned Si. (note: the raw XPS spectra are presented in Fig.S2). The Si sample had about 20% adventitious hydrocarbon (red and black) on the surface after the native oxide removal using an aqueous HF. 0.25 MegaL of MoF₆ were dosed at 120 °C and 12% Mo and 28% F were deposited. All of the Mo was in oxidation states of +4 and +5 consistent with MoF_x termination of the surface. MoF₆ has a self-limiting reaction on HF cleaned Si, and 0.25 MegaL of MoF₆ was the saturated dose of MoF₆ on Si at 120 °C. [20] 26.4 MegaL of Si₂H₆ was dosed on MoF₆ saturated Si surface which reduced MoF_x to Mo (0) by forming Mo-Si bonds consistent with MoSix deposition. The 11% oxidized component of Si (grey bar) and 4% oxidized Mo component (purple bar) might be due to the O and F contamination at the surface. Subsequently, 3.5 MegaL of O_2 was dosed which increased O from 17% to 26%; however, the oxidized component of Mo remained 4% out of a total of 8%. After another 4.3 MegaL of O2 was dosed at 120 °C, O increased only by 2% and the oxidized component of Mo increased to 6% out of a total of 8%. At 120 °C, reactivity of O₂ with a MoSiO_x monolayer was insufficient to completely oxidize MoSi_x. In Fig. 2(b), the same sample was employed to investigate higher temperature (200 °C) reaction with O2. 4.3 MegaL O2 at 200 °C was able to fully oxidize Mo, the oxidized component of Si



Fig. 4. Surface morphologies of HF cleaned Si and SiO₂ after 3 step ALD MoSiO_x deposition. (a) AFM image of the as-deposited MoSiO_x film on HF-Si was atomically flat. (b) AFM after an in-situ O₂/He anneal at 300 °C/MoSiO_x/HF-Si showed a conformal film. (c) After an ex-situ O₂ anneal at 350 °C, the MoSiO_x surface on HF-Si was roughened with ~6 nm tall agglomerations. (d) SiO₂ after the MoSiO_x ALD cycles followed by an in-situ O₂/He anneal at 300 °C shows a flat SiO₂ surface without any MoSiO_x nuclei.

increased from 14% to 16%, and the O increased from 28% to 32% consistent with a complete conversion of $MOSi_x$ into $MOSiO_x$. After 3 additional ALD cycles at 200 °C, the total thickness of the $MOSiO_x$ film on Si was ~2.2 nm calculated from the attenuation of the Si substrate. In contrast, during the same exposure of MoF_6 , Si_2H_6 , and O_2 at 120 °C and 200 °C, HF cleaned SiO_2 remained non-reactive which is consistent with the inherent non-reactivity of the SiO_2 surface against these precursors. (Fig. 2(b))

After the MoSiO_x ALD cycles at 120–200 °C, in-situ and ex-situ post deposition anneals (PDA) in O₂ were performed to further oxidize the film. (note: the raw XPS spectra are presented in Fig. S3). Fig. 3(a) shows the XPS elemental compositions after each O₂ PDA step and Fig. 3(b,c) presents the corresponding oxidation states of Mo 3d and Si 2p. As deposited MoSiO_x had oxidation states of Mo¹⁺ and Mo³⁺. Si had Si⁴⁺ and Si⁰. Note that Si⁰ component corresponds to the Si substrate peak. An in-situ O₂/He anneal was performed on MoSiO_x/HF-Si at 300 °C for 6 mins at a constant flow of O₂/He at 80–150 mTorr. This corresponds to 432 MegaL of O₂. After the in-situ O₂/He anneal, F at the surface went down from 16% to 3% and O went up from 36% to 43% consistent with a substitution of surface F with O. However, the oxidation states of Mo still contained a large fraction of Mo¹⁺. Therefore, an ex-situ oxidation at ~1 atm was performed for 10 mins at 350 °C using an AllWin21 rapid thermal annealing system with a constant



Fig. 5. XP S elemental percentage of Si and Mo and the MoSiO_x film thickness on Si and SiO₂ for 3 step ALD MoSiO_x. (a) The Si substrate peak (Si(0)) was attenuated as the number of cycles increased while the SiO₂ substrate peak (Si (ox)) remained the constant which is consistent with the selective growth of MoSiO_x deposition. (b) The growth of MoSiO_x on Si was limited up to 5.25 \pm 0.5 nm. There was no growth of MoSiO_x on SiO₂. The film thicknesses were calculated using the attenuation of the substrates.

100% O₂ flow at 1 SLM at about 1 atm. This corresponds to 456 GigaL of O₂. After the ex-situ anneal, the sample was introduced back into the UHV chamber to analyze the compositions and oxidation states. The elemental composition showed a large amount of surface C and O which have resulted from the air exposure during transfer. However, the oxidation states of both Mo 3d and Si 2p were consistent with fully oxidized MoSiO_x. The could be due to either the higher temperature or $\sim 10^3 \times$ larger dose of O₂ compared to the in-situ O₂/He anneal at 300 °C. Below, it is shown that the film can be fully oxidized (as quantified by XPS) by an in-situ anneal in O₂/He at at 15 Torr at 350 °C.

The surface morphologies of the deposited MoSiO_v film from 3 step ALD were studied using atomic force microscopy (AFM) for as-deposited, after an in-situ O2/He anneal at 300 °C, and after ex-situ O2 anneal at 350 °C. Fig. 4(a) shows the surface morphology of the asdeposited 3 step ALD MoSiOx on Si after the 4 ALD cycles at 120-200 °C. The MoSiO_x film was atomically flat with an RMS roughness of 5.3 Å. Fig. 4(b) depicts the 3 step ALD MoSiO_x surface after an in-situ O2/He anneal at 15 torr at 300 °C to further oxidize the unsaturated MoSiO_x film. The film was smoother after the anneal with an RMS roughness of 3.8 Å. Fig. 4(c) shows an AFM image of the 3 step ALD MoSiO_x surface after the ex-situ O₂ anneal at \sim 1 atm at 350 °C for 10 mins. The surface after the ex-situ anneal was roughened and had \sim 6 nm tall agglomerations which might be due to the large insertion of oxygen. The RMS roughness was 1.6 nm. To check the selectivity of MoSiO_x on SiO₂. AFM was performed on HF cleaned SiO₂ after 4 ALD cycles of 3 step ALD MoSiOx followed by an in-situ O2/He anneal at 300 °C (see Fig. 4(d)). The SiO₂ surface was very clean with an RMS roughness of 5.3 Å. There was no MoSiOx nucleation or particle formation observed on the surface which shows the absolute inherent selectivity of the MoSiOx ALD on SiO2.

To study the selectivity and growth rate of 3 step ALD $MOSiO_x$ with XPS, thicker films were deposited on Si and SiO_2 . A total of 20 ALD cycles of 3 step ALD $MOSiO_x$ at 200 °C were performed and the film



Fig. 6. Elemental compositions at each deposition step of 2 Step $MoSi_x + in-situ O_2/He$ anneal on Si and SiO₂. (a) 5 ALD cycles of MoF₆ and Si₂H₆ at 120 °C followed by an in-situ O₂/He anneal at 350 °C were performed on HF cleaned Si. (b) 5 ALD cycles of MoSi_x ALD at 120 °C and an in-situ O₂/He anneal at 350 °C on HF cleaned SiO₂. (c) The raw Mo 3d XPS spectra after MoSi_x deposition at 120 °C followed by the in-situ O₂/He anneal at 15 Torr at 350 °C. (d) The raw Si 2p XPS spectra after MoSix deposition at 120 °C followed by the in-situ O₂/He anneal at 15 Torr at 350 °C.

thickness was calculated by the attenuation of the substrate after each 5 ALD cycles. (note: the raw XPS spectra are presented in Fig. S4). Fig. 5(a) presents the elemental percentage of Si and Mo from the Si and SiO₂ substrates for up to 20 ALD cycles at 200 °C. As the number of cycles increases, the Si(0) percentage from the Si substrate decreases which is consistent with the attenuation of Si due to the MoSiO_x growth. The Mo percentage on the Si substrate was saturated at ~20% after 5 ALD cycles consistent with the composition of the MoSiO_x film being conformal throughout the film. In contrast, Si(ox) of SiO₂ which corresponded to the SiO₂ substrate remained at ~40% throughout the 20 ALD cycles which is consistent with no MoSiO_x deposition. A negligible amount of Mo was detected on the SiO₂ substrate.

Fig. 5(b) shows the $MoSiO_x$ film thickness on Si and SiO_2 as a function of the number of ALD cycles. After the first 5 ALD cycles, the thickness of $MoSiO_x$ on Si was 3.30 \pm 0.35 nm which corresponds to a growth rate of 6.6 Å/cycle. The second set of 5 ALD cycles (up to 10th



Fig. 7. Surface morphologies of 2 Step ALD $MoSiO_x$ before and after the in-situ O_2 /He anneal at 350 °C and its electrical properties. (a) The surface morphology of an as-deposited $MoSi_x$ film on Si. (b) The surface morphology of $MoSiO_x$ after the in-situ O_2 /He anneal at 350 °C. (c) I-V curve of the $MoSiO_x$ film. (d) G-V curve of the $MoSiO_x$ film. Sweeping mode from 10 kHz to 1 MHz frequency was used at -2 to 2 V gate bias.

cycle) and the third set (up to 15th cycle) shows slower growth rates of 2.8 and 1.1 Å/cycle. After the 15th ALD cycle, there was no additional growth of $MoSiO_x$ on Si. Overall, $MoSiO_x$ on Si showed a logarithmic growth and saturated at 5.25 ± 0.5 nm. The larger growth rate of $MoSiO_x$ during the first 5 ALD cycles might be due to MoF_6 reacting more than a monolayer of the Si substrate. As the film grew, the substrate effect became smaller and the growth rate decreased. After 15 ALD cycles, the $MoSiO_x$ film became inert to both MoF_6 and Si_2H_6 due to the strong bonds of Mo-O and Si-O which terminate the reaction. Conversely, there was no growth observed on SiO_2 for up to 20 ALD cycles.

Selectivity of $MoSiO_x$ ALD on SiO_2 was calculated from XPS sensitivity. After a total of 20 ALD cycles, there were 1.9% Mo and 6.4% F detected on SiO_2 by XPS. Assuming all of Mo and F were conformally covering the topmost surface of SiO_2 , this corresponds to less than 0.5 Å thick film calculated using the inelastic mean free path (IMFP) of electron and electron attenuation length (AL) as follows:

 $\lambda = \frac{143}{\mathrm{E}^2} + 0.054\sqrt{\mathrm{E}}$

 $I = I_0 \exp(-t/\lambda \sin\theta),$

where λ is an IMFP of electron, E is a kinetic energy of electron, I is an attenuation length (AL), I_0 is a constant, t is a thickness (layer depth) and θ is an angle of emitted electron from the surface. Assuming a monolayer of the MoSiO_x film is ~ 3 Å, MoSiO_x on SiO₂ after 20 ALD



Fig. 8. XPS elemental composition and SEM images of a patterned sample before and after selective 2 Step ALD $MOSiO_x + PDA$ deposition. (a) HF cleaned patterned sample mostly has SiN and Si(0) components. (b) After the selective $MOSiO_x$ deposition, there was $MOSiO_x$ together with SiN. (c) A top view SEM image of the HF cleaned patterned sample shows that the patterned sample had ~50 nm and ~30 nm trough structure. The insert is a schematic of the cross sectional patterned sample. (d) SEM image of the patterned sample after the $MOSiO_x$ deposition. The insert is a schematic of the cross sectional patterned sample. After ALD, the patterned sample had ~60 nm and ~20 nm trough structure consistent with 5 nm of ALD on the side walls.

cycles was calculated to 0.167 monolayer. As the $MoSiO_x$ film on Si after 20 ALD cycles was estimated to 5.25 nm, which corresponds to 17.5 monolayers, the selectivity of $MoSiO_x$ between Si and SiO_2 is at least 100:1 consistent with the more sensitive AFM determination of selectivity.

To overcome the growth limit, a second technique of selective MoSiO_x deposition was investigated which was to selectively deposit MoSix using MoF₆ and Si₂H₆ at 120 °C and then convert the MoSix film into MoSiO_x via an in-situ O₂/He anneal at 350 °C at 15 Torr. Fig. 6 shows the XPS composition of a new batch of HF cleaned Si and HF cleaned SiO₂ samples for the second technique denoted as "2 Step ALD". HF cleaned Si had ~20% hydrocarbon on the surface. After 5 ALD cycles of MoF₆ and Si₂H₆ to deposit MoSi_x at 120 °C, the composition of the film was 31% Mo, 16% Si, 23% O and 29% F consistent with previous experiments. [20] A saturation study of MoF₆ and Si₂H₆ at 120 °C was also performed and shown in Fig. S7. Note that Mo(ox) was only 7% out of 31% consistent with metallic Mo-Si bond formation of MoSi_x. After an in-situ O₂/He (10% balanaced in He) anneal at 15 Torr for 10 mins at 350 °C, All of Mo was oxidized, and the film surface was mostly MoO_x with only 4% Si. The data is consistent with the 350 °C O₂ anneal inducing loss of fluorine from the surface via SiF_x desorption and formation of additional Mo-O bonds. To study the bulk composition of the film, near normal XPS (60° take-off angle from the sample surface) was performed. (see Fig. 6(a)) The bulk of the film had a Mo:Si:O ratio of 1: 0.8: 1.9 which is consistent with the in-situ O_2 /He anneal segregating MoO_x on the surface of the film. This is consistent with the lower



Fig. 9. Cross-sectional TEM image of the patterned sample before and after the selective 2 Step ALD $MoSiO_x + PDA$ deposition. (a) The patterned sample had Si fins covered with a SiN mask. There was a SiO₂ interlayer in between. (b) After the 5% HF clean followed by the $MoSiO_x$ deposition, $MoSiO_x$ was selectively deposited on the sidewalls of the Si fins. Note that a wet etch in 5% HF solution before the $MoSiO_x$ deposition etched the SiN and SiO₂ features.

surface free energy of MoO_3 compared to SiO_2 (MoO_3 : 70 ergs/cm₂ versus SiO_2 : 307 ergs/cm²).

HF cleaned SiO₂ has a negligible amount of C at the surface as presented in Fig. 6(b). (note: the raw XPS spectra are presented in Fig. S5). After 5 cycles of MoSi_x ALD at 120 °C, there was 1.5% Mo and 8% F detected on the surface. After an in-situ O2/He anneal at 350 °C, there was no change but a small decrease in F which is consistent with the inherently non-reactivity of MoSiOx on HF-SiO2. The selectivity estimation using XPS sensitivity was also performed for 2 step ALD. There were 1.5% Mo and 5% F observed on SiO2 after 5 ALD cycles of MoSix followed by the in-situ O₂/He anneal at 350 °C. This corresponds to a 0.5-thick conformal film which is 0.167 monolayer assuming 1 monolayer is 3 Å. The thickness of MoSiOx on Si after the same deposition deposited was about 6 nm MoSiO_x (~20 monolayers of MoSiO_x) so that the selectivity of 2 step ALD was estimated to about 120:1. Fig. 6(c) presents the Mo 3d XPS spectra showing the oxidation states before and after the in-situ O₂/He anneal. After 5 ALD cycles of MoF₆ and Si₂H₆ at 120 °C, Mo was mostly Mo⁰ consistent with metallic MoSi_x being deposited. After the in-situ O2/He anneal at 350 °C, Mo 3d peaks were shifted to Mo⁴⁺ and Mo⁵⁺ which corresponded to oxidized MoSiO_x. Fig. 6(d) shows the Si 2p XPS spectra before and after the in-situ O₂/He anneal. Before the in-situ O2/He anneal, Si had two oxidation states of Si(0) and Si(4). Si(0) corresponds to Mo-Si bonds from MoSi_x and Si(4) component is due to the surface F and O contamination. After the insitu O₂/He anneal at 350 °C, all of Si at the surface was at an oxidation state of 3 consistent with a full conversion to MoSiO_x.

In Fig. 7, the surface morphology of $MoSiO_x$ before and after the insitu O_2 /He anneal at 350 °C are shown. The surface morphology of $MoSi_x$ was smooth with an RMS roughness of 6.9 Å (Fig. 7(a)). After an in-situ O_2 /He anneal at 350 °C, the $MoSiO_x$ surface remained smooth with an RMS roughness of 1.0 nm (Fig. 7(b)). The slight increase of the RMS roughness can be attributed to the O_2 incorporation. To investigate the electrical properties of the MoSiO_x film, a Ni gate on top of MoSiO_x with an Al back contact were deposited via thermal evaporation. Fig. 7(c,d) depicts the current density-voltage (I-V) and conductance density–voltage (G-V) curves. The current density through the MoSiO_x film in the gate bias range was smaller than $\sim 1 \times 10^{-7}$ A and the conductance density was constant across the gate bias which are both consistent with an insulating MoSiO_x film.

Using inherently selective processes, a selective and conformal deposition of $MOSiO_x$ was demonstrated on a three-dimensional nanotrench structure with a high-aspect ratio. The structure of the patterned sample is described in Fig. 8(c). The Si fins are 225 nm tall and 50 nm wide with SiN mask on top of each Si fin separated by SiO₂.

Fig. 8(a) shows the elemental composition of the HF cleaned patterned sample. (note: the raw XPS spectra are presented in Fig. S6). The patterned sample had mostly SiN on the top-most surfaces. Note that there is 18% Si (0) which corresponds to the target area for MoSiO_x deposition since the oxidized Si peak corresponds to the exposed SiN and SiO_2 surfaces. Fig. 8(b) shows the elemental composition after a selective MoSiO_x deposition process. There was 8% fully oxidized Mo with 21% O. Note that all of the Si was oxidized consistent with a selective attenuation of the Si substrate (Si(0) component, the target area). The patterned sample shown in Fig. 8(c) is a top view SEM image of the HF cleaned patterned sample. The SiN mask was 50 nm wide and the gap between the SiN mask was 30 nm which is also shown in the insert on the left bottom corner. Fig. 8(d) shows the same region as Fig. 8(c) after the selective $MoSiO_x$ deposition. The gap between the features decreased to 20 nm and the SiN mask rows were enlarged to ${\sim}60\,\text{nm}$ which is consistent with ${\sim}5\,\text{nm}$ thick MoSiO_x deposition on each sidewall of the Si fins.

Fig. 9 shows the cross sectional TEM images of the patterned sample before and after the selective $MoSiO_x$ deposition process. Fig. 9(a) shows the structure of the patterned sample. The patterned sample was

cleaned using 5% HF solution for 30 s and selective $MoSiO_x$ deposition was performed. Unlike the 0.5% HF solution that was used for the blanket Si and SiO₂ samples, 5% HF solution was used for the patterned sample in order to remove a protective layer over the SiN/SiO₂/Si fin structures. 5% HF solution was 10 times more concentrated than what it is required to remove a native oxide on the Si fins so that the SiN mask and SiO₂ layer were etched together. However, $MoSiO_x$ was still very conformal and selective on Si. The deposited $MoSiO_x$ film was ~6 nm thick. The gap between each fin was ~20 nm which is consistent with the SEM image in Fig. 8(d). The TEM image demonstrates that the highly selective $MoSiO_x$ can be achieved on a patterned sample and be integrated into three-dimensional nanoscale multi-patterning processes.

4. Conclusion

A new approach to selectively deposit oxides on Si in preference to SiO₂ and SiN was demonstrated by two different inherently selective MoSiO_x ALD processes using MoF₆, Si₂H₆ and O₂. Alternatingly dosed MoF₆, Si₂H₆ and O₂ at 200 °C (3 Step ALD) deposited an oxygen-deficient MoSiO_x film on Si with perfect selectivity over SiO₂ quantified by AFM. The selectivity estimated by XPS presented at least 100:1 between Si and SiO₂. An ex-situ anneal in 100% O₂ at 350 °C could fully oxidized the film. The growth of MoSiO_x on Si was limited up to 5 nm due to the inherent non-reactivity of the precursors towards the grown MoSiO_x which demonstrates the strong substrate-dependent nature of MoSiO_x ALD. For the thicker films, selective 2 step $MoSi_x$ ALD was employed before a conversion of the MoSi_x film into MoSiO_x by an in-situ O₂/He anneal. Loss of selectivity was not observed on SiO2 until 10 nm of MoSi_x was grown on Si which could expand the selectivity to 200:1. The selectivity of the process relies on the inherent selectivity of MoSix ALD using MoF₆ and Si₂H₆ which deposits on Si but not on SiO₂ or SiON. It has been shown that this process is selective because of the weak Si-Si and H-Si bonds on Si and the ease of formation of SiF₄ on a Si substrate but the stronger Si-O, Si-N, SiO-H and SiN-H bonds in SiO₂ and SiN make this process less favorable. The conversion of metal or metal silicide into an oxide film is advantageous in terms of selectivity in that the process does not require any use of strong oxidants such as H₂O, H₂O₂ and O₂ plasma during the deposition which often leads to selectivity loss. For the selective ALD of metal or metal silicides such as MoSi_x, W, Mo, Co and CoSi₂, reductants are employed which utilize an inherent surface-dependent selectivity and subsequently convert them into oxides by an O2 PDA. Selective MoSiOx deposition on the sidewalls of Si fins in nanoscale demonstrated a great potential application in three-dimensional nanoscale multi-patterning processes.

Acknowledgements

Funding support from Applied Materials is gratefully acknowledged. The electrical measurements were facilitated by the San Diego Nanotechnology Infrastructure (SDNI) which is supported by the National Science Foundation (NSF) to Nano3 (Grant ECCS-1542148).

Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.apsusc.2019.144307.

References

- A.J.M. Mackus, A.A. Bol, W.M.M. Kessels, The use of atomic layer deposition in advanced nanopatterning, Nanoscale 6 (2014) 10941–10960.
- [2] L. Li, X. Liu, S. Pal, S. Wang, C.K. Ober, E.P. Giannelis, Extreme ultraviolet resist materials for sub-7 nm patterning, Chem. Soc. Rev. 46 (2017) 4855–4866.
- [3] J.A. DeFranco, B.S. Schmidt, M. Lipson, G.G. Malliaras, Photolithographic patterning of organic electronic materials, Organic Electronics 7 (2006) 22–28.
- [4] S. Liu, A. Al-Shadeedi, V. Kaphle, C.-M. Keum, B. Lüssem, Patterning organic transistors by dry-etching: the double layer lithography, Organic Electronics 45 (2017) 124–130.
- [5] K.R. Williams, K. Gupta, M. Wasilik, Etch Rates for Micromachining Processing—Part II, J. Microelectromech. Syst. 12 (2003) 761–778.
- [6] A.J.M. Mackus, M.J.M. Merkx, W.M.M. Kessels, From the bottom-up: toward areaselective atomic layer deposition with high selectivity, Chem. Mater. 31 (2019) 2–12.
- [7] X. Liu, S. Ramanathan, A. Longdergan, A. Srivastava, E. Lee, T.E. Seidel, J.T. Barton, D. Pang, R.G. Gordonb, ALD of hafnium oxide thin films from tetrakis(ethylmethylamino)hafnium and ozone, J Electrochem. Soc. 152 (2005) G213–G219.
- [8] S.W. Park, J.Y. Choi, S. Siddiqui, B. Sahu, R. Galatage, N. Yoshida, J. Kachian, A.C. Kummel, Formation of atomically ordered and chemically selective Si—O—Ti monolayer on Si_{0.5}Ge_{0.5}(110) for a MIS structure via H₂O₂(g) functionalization, J. Chem. Phys. 146 (2017).
- [9] H.B. Profijt, P. Kudlacek, M.C.M. van de Sanden, W.M.M. Kessels, Ion and photon surface interaction during remote plasma ALD of metal oxides, J. Electrochem. Soc. 158 (2011) G88–G91.
- [10] X. Wang, S.M. Tabakman, H. Dai, Atomic layer deposition of metal oxides on pristine and functionalized graphene, J. Am. Chem. Soc. 130 (2008) 8152–8153.
- [11] J. Hamalainen, F. Munnik, M. Ritala, M. Leskela, Atomic layer deposition of platinum oxide and metallic platinum thin films from Pt(acac)2 and ozone, Chem. Mater. 20 (2008) 6840–6846.
- [12] J.A. Singh, N.F.W. Thissen, W.-H. Kim, H. Johnson, W.M.M. Kessels, A.A. Bol, S.F. Bent, A.J.M. Mackus, Area-selective atomic layer deposition of metal oxides on noble metals through catalytic oxygen activation, Chem. Mater. 30 (2018) 663–670.
- [13] M. Ritala, K. Kukli, A. Rahtu, P.I. Raisanen, M. Leskela, T. Sajavaara, J. Keinonen, Atomic layer deposition of oxide thin films with metal alkoxides as oxygen sources, Science 288 (2000) 319–321.
- [15] A. Mameli, M.J.M. Merkx, B. Karasulu, F. Roozeboom, W.M.M. Kessels, A.J.M. Mackus, Area-selective atomic layer deposition of SiO₂ using acetylacetone as a chemoselective inhibitor in an ABC-type cycle, ACS Nano 11 (2017)

J.Y. Choi, et al.

9303-9311.

- [16] F.S.M. Hashemi, S.F. Bent, Sequential regeneration of self-assembled monolayers for highly selective atomic layer deposition, Adv. Mater. Interf. 3 (2016) 1600464.
- [17] R. Vallat, R. Gassilloud, B. Eychenne, C. Vallée, Selective deposition of Ta2O5 by adding plasma etching super-cycles in plasma enhanced atomic layer deposition steps, J. Vac. Sci. Technol. A 35 (2017) 01B104.
- [18] C. Prasittichai, K.L. Pickrahn, F.S.M. Hashemi, D.S. Bergsman, S.F. Bent, Improving area-selective molecular layer deposition by selective SAM removal, ACS Appl.

Mater. Interf. 6 (2014) 17831-17836.

- [19] S.E. Atanasov, B. Kalanyan, G.N. Parsons, Inherent substrate-dependent growth initiation and selective-area atomic layer deposition of TiO₂ using "water-free" metal-halide/metal alkoxide reactants, J. Vac. Sci. Technol. A 34 (2016) 01A148.
- [20] J.Y. Choi, C.F. Ahles, R. Hung, N. Kim, A.C. Kummel, Selective atomic layer deposition of MoSix on Si (001) in preference to silicon nitride and silicon oxide, Appl. Surf. Sci. 462 (2018) 1008–1016.