W deposition and titanium fluoride formation during WF₆ reduction by Ti: Reaction path and mechanisms

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Reaction of WF₆ with air-exposed 27- and 250-nm-thick Ti films has been studied using Rutherford backscattering spectroscopy, scanning and high-resolution transmission electron microscopy, electron and x-ray diffraction, and x-ray photoelectron spectroscopy. We show that W nucleates and grows rapidly at localized sites on Ti during short WF₆ exposures (~6 s) at 445 °C at low partial pressures $p_{WF_6} < 0.2$ Torr. Large amounts of F, up to $\approx 2.0 \times 10^{17}$ atoms/cm$^2$ corresponding to an average F/Ti ratio of 1.5 in a 27-nm-thick Ti layer, penetrate the Ti film, forming a solid solution and nonvolatile TiF₃. The large stresses developed due to volume expansion during fluorination of the Ti layer result in local delamination at the W/Ti and the Ti/SiO$_2$ interfaces at low and high WF$_6$ exposures, respectively. WF$_6$ exposure at $p_{WF_6} > 0.35$ results in the formation of a network of elongated microcracks in the W film which allow WF$_6$ to diffuse through and attack the underlying Ti, consuming the 27-nm-thick Ti film through the evolution of gaseous TiF$_4$. © 1999 American Institute of Physics. [S0021-8979(99)10303-7]

I. INTRODUCTION

W chemical vapor deposition (CVD) from WF$_6$—the process of choice for filling high aspect ratio holes in ultralarge-scale integrated (ULSI) circuits$¹–⁶$—requires the use of conformal TiN/Ti bilayers. TiN is used as a diffusion barrier to prevent WF$_6$ reaction with underlying layers,$⁷–¹⁰$ and Ti getters interfacial oxygen from the surface of the underlayers (e.g., Al) to reduce via resistance. On substrates such as Si and SiO$_2$, Ti also serves as an adhesion promoter by reacting to form a thin TiSi$_2$ layer.$¹¹,¹²$

Delamination of sputter-deposited TiN/Ti liners during W CVD is a serious problem in the fabrication of sub-0.35 μm ULSI structures.$¹¹–¹⁴$ Recently,$¹⁵–¹⁸$ we showed that such delamination is caused by WF$_6$ diffusing through nanopipes in underdense TiN layers, injecting F into the underlying Ti layer during W nucleation, and weakening the Ti/SiO$_2$ interface. To better understand the delamination mechanism, we study the microchemical changes and phase formation occurring in the Ti layer, especially in regions of poor TiN coverage in high-aspect ratio device features where Ti is directly exposed to the incoming flux of WF$_6$ molecules. Developing an understanding of F penetration into Ti is also important in order to evaluate the stability of Ti when in contact with F-containing compounds such as fluorinated silicon glass (FSG), parylene, fluorinated amorphous carbon (FLAC) etc., candidate materials for low-k dielectric applications in sub-0.25 μm devices.

It is generally known that WF$_6$ reacts more rapidly with Ti surfaces than TiN.$¹⁹–²³$ However, the pathway for WF$_6$ reaction with Ti and the phase formation sequence are not well understood. In fact, this reaction has been addressed only perfunctorily in reports devoted to studies of other phenomena. Some researchers$²⁴,²⁵$ have speculated on volatile TiF$_4$ formation while others have suggested nonvolatile TiF$_3$ formation.$¹⁹–²³$ Barber and Shenasa$²⁴$ inferred volatile fluoride formation from their Auger electron spectroscopy data, which did not contain any Ti or F peaks following WF$_6$ exposure of Ti. Based upon bright-field transmission electron microscopy (TEM) micrographs, Broadbent and co-workers$¹⁹,²⁰$ suggested the formation of TiF$_3$. However, there was no structural information presented to identify the fluoride phase formed. Yu, Ahn, and Joshi$²²,²³$ assumed TiF$_3$ formation due to a large shift in the Ti $2p$ x-ray photoelectron spectroscopy (XPS) peak when a “clean” Ti surface was exposed to WF$_6$ at room temperature. Since other nonvolatile titanium fluorides$²⁶$ and oxyfluorides$²⁷$ are also known to exist and may give rise to a similar peak shift, phase identification is not conclusive in the absence of structural information.

In this article, the reaction of WF$_6$ with Ti is systematically examined as a function of WF$_6$ dose and the phase formation sequence is revealed. We show that Ti rapidly reduces WF$_{6φ}$, resulting in W deposition and F injection into the Ti layer. At low average F concentrations in the Ti film, $C_F$ up to $\approx 10$ at. %, a Ti–F solid solution forms. Increasing $C_F$ results first in the formation of TiF$_3$ followed by the release of gaseous TiF$_4$. Microcracks in the deposited W overlayer not only allow incident WF$_6$ molecules to diffuse

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through them and continue the attack on the Ti underlayer, but also serve as facile paths for TiF$_4$ evolution. The phase formation sequence is discussed based upon thermodynamic arguments and a phenomenological model is proposed.

II. EXPERIMENTAL PROCEDURE

Ti films of two different thicknesses, 27 and 250 nm, were grown at 250°C by magnetron sputter deposition in an Applied Materials Endura HP process tool on 700-nm-thick SiO$_2$ layers deposited by plasma enhanced CVD on 200-mm-diam Si(001) wafers. The base pressure in the deposition chamber was $1 \times 10^{-8}$ Torr. Ti deposition was carried out in Ar at 5 mTorr, yielding a deposition rate of 2.2 nm s$^{-1}$. All samples were exposed to air before being loaded into a Novellus Systems Concept One cold-wall CVD reactor where they were exposed to WF$_6$ gas at 445°C for 6 s in an Ar/WF$_6$ mixture with an Ar flow rate of 12000 sccm and a total pressure of 40 Torr. The WF$_6$ dose was varied by changing the WF$_6$ partial pressure $p_{WF_6}$ from 0.2 to 1.3 Torr.

Rutherford backscattering spectroscopy (RBS) was used to monitor compositional changes in the reacted Ti layers. The RBS probe beam consisted of 2 MeV $^4$He$^+$ ions incident at angles between $-10^\circ$ and $30^\circ$ to the sample normal and the detector was set at a scattering angle of $150^\circ$. Angle-resolved RBS was used to distinguish between, and identify the location of, light elements such as O and F. The spectra were analyzed through comparisons with RUMP$^{28}$ computer simulations.

Elemental chemical-state information was obtained using XPS. The measurements were performed in a Perkin Elmer PHI 5400 system equipped with a Mg K$\alpha$ X-ray source. Elemental binding energies were calibrated using Cu and Au standards. Surface impurities such as carbon were also used as internal references. The Ti 2$p$ peaks were deconvoluted by nonlinear least-squares curve fitting using the PHI 5000 Series-electron spectroscopy for chemical analysis (ESCA) version 4.1A computer software.

Film morphology was investigated using secondary and Z-contrast scanning electron microscopy (SEM) in Hitachi S 800 and Zeiss 960 microscopes operated at 20 kV. Plan-view TEM was carried out in a Philips CM 12 microscope at 120 kV to characterization the microstructure of the Ti film prior to, and after, WF$_6$ exposures. Structure and morphology of phases formed were investigated using conventional and high-resolution TEM (HRTEM), electron diffraction, and x-ray diffraction (XRD). A Rigaku DMAX-III diffractometer with a monochromatic Cu K$\alpha$ X-ray source was used for the XRD measurements.

III. RESULTS

A. W nucleation and morphology

Ti films exposed to WF$_6$ for 6 s at various partial pressures $p_{WF_6}$ were examined by SEM. Figure 1(a) shows a typical micrograph of a sample exposed to WF$_6$ at $p_{WF_6} = 0.2$ Torr. Spherical W particles (average size 111 ± 70 nm) form at local sites on the Ti film. The particles appear in the micrograph as spheres of bright contrast, identified to be W by Z-contrast SEM and energy dispersive x-ray spectroscopy (EDX). Microcracks were observed in the larger W particles when $p_{WF_6}$ was ≧0.35 Torr. This is clearly seen in Fig. 1(b), a representative SEM micrograph of a sample exposed to WF$_6$ at $p_{WF_6} = 0.35$ Torr. Further increases in $p_{WF_6}$ resulted in the formation of a very rough W film with elongated microcracks extending across the film [see Fig. 2(a)]. The observed morphology is similar to that reported by Broadbent and co-workers during WF$_6$ reduction by TiSi$_2$. Examination of WF$_6$-exposed Ti films on patterned SiO$_2$ substrates revealed that microcrack formation is more pronounced near the top edges of topological features such as trenches and via holes. An example is shown in Fig. 2(b).

The W overlayers exhibit local delamination even in flat areas of the sample. Examination of these regions by Z-contrast SEM (Fig. 3) and EDX revealed the presence of a thin W layer on which the spherical W particles are dispersed. The particles appear brighter than the W layer because their average diameter is much larger than the W layer thickness. These results suggest that a thin continuous W layer is deposited on Ti prior to preferential WF$_6$ reduction, which leads to the formation of the large W particles.

B. Fluorine incorporation and Ti etching

WF$_6$-exposed Ti/SiO$_2$ samples were analyzed by RBS in order to follow compositional changes in the Ti film as a function of partial pressure. Figure 4 shows typical RBS spectra from samples exposed to WF$_6$ for 6 s at $p_{WF_6}$ values...
between 0 and 0.55 Torr. The O peak at \( \approx 0.77 \) MeV in the as-deposited sample results from a 7-nm-thick native oxide on the Ti film, while the roughness of the W overlayer gives rise to the tail in the trailing edge of the W peak. RUMP simulations revealed that the large peaks at \( \approx 0.90 \) MeV superimposed on the Si substrate signal in the WF\(_6\)-exposed samples correspond to \( \approx 2.0 \times 10^{17} \) and \( 8.0 \times 10^{16} \) atoms/cm\(^2\) F in the Ti layers with \( p_{WF_6} = 0.20 \) and 0.55 Torr, respectively. This peak is absent in the as-deposited Ti/SiO\(_2\) sample, and is easily distinguished from the surface O peak by comparing angle-resolved RBS spectra.

W, Ti, and F concentrations obtained by fitting RBS spectra using RUMP simulations are plotted as a function of \( p_{WF_6} \) in Fig. 5. The nominal thickness of each layer was estimated assuming theoretical density. The W film thickness was found to increase monotonically with \( p_{WF_6} \) while the Ti thickness initially decreased by \( \approx 3 \) nm at \( p_{WF_6} = 0.2 \) Torr and remained relatively unchanged for WF\(_6\) exposures up to \( p_{WF_6} = 0.35 \) Torr. Further increases in \( p_{WF_6} \) from 0.35 to 1.3 Torr resulted in the Ti thickness decreasing sharply from 24 to \( \approx 0.13 \) nm, indicating that Ti is rapidly etched at high WF\(_6\) exposures. The consumption of the Ti film at high \( p_{WF_6} \) is illustrated by the RBS spectra in Fig. 6 which shows that the integrated Ti peak intensity in samples exposed to WF\(_6\) at \( p_{WF_6} = 1.3 \) Torr is about two orders of magnitude lower than the corresponding intensity measured for the 27-nm-thick Ti layer in the as-deposited sample. Note the presence of the W film despite the removal of the Ti underlayer. This observation is also supported by the SEM micrograph shown in Fig. 3.

The total amount of incorporated F is not a strong function of \( p_{WF_6} \) below 1.3 Torr, the WF\(_6\) partial pressure at which the F peak disappears completely. However, the F/Ti ratio increases gradually from 1.5 to 2.4 as \( p_{WF_6} \) is increased from 0.2 to 0.55 Torr. From the simultaneous loss of F and Ti at high WF\(_6\) partial pressures, it is evident that F is present predominantly in the Ti layer rather than in the W overlayer. The F/W ratio, calculated from the RBS data in Fig. 5, is \( 6 \pm 0.7 \) at \( p_{WF_6} < 0.35 \) Torr indicating that at low WF\(_6\) exposures essentially all F atoms from dissociated WF\(_6\) molecules react and diffuse into the bulk of the Ti film. As \( p_{WF_6} \) increases to 0.55 Torr, the F/W ratio decreases to \( \approx 3(\pm 1) \) suggesting the evolution of F-containing volatile product species.

C. TiF\(_3\) formation

The above results show that gaseous titanium fluoride is not a major reaction product at \( p_{WF_6} < 0.35 \) Torr as evidenced by the relatively small Ti loss compared to the rapid Ti removal observed at higher WF\(_6\) exposures. A combination of TEM, XRD, and XPS was used to investigate nonvolatile phase formation in WF\(_6\)-exposed Ti/SiO\(_2\) samples with \( p_{WF_6} < 0.35 \) Torr.

Figure 7(a) is a representative HRTEM micrograph from a Ti/SiO\(_2\) sample exposed at \( p_{WF_6} = 0.2 \) Torr. The presence of \( \approx 20 \)-nm-sized domains of a second phase dispersed in the Ti matrix is clearly revealed. A magnified view of a second phase domain is shown in Fig. 8. The interplanar separations and orientation of the lattice planes are consistent with the
(011\bar{2}), (10\bar{1}4), and (1\bar{1}02) planes of hexagonal TiF₃ (Ref. 29), as viewed along the [20\bar{1}T] zone axis. Selected-area electron diffraction (SAED) patterns showing azimuthally continuous (011\bar{2}), (02\bar{2}4), and (30\bar{3}0) TiF₃ diffraction rings indicate that the TiF₃ domains do not have any in-plane preferred orientation. A typical SAED pattern is shown in Fig. 7(b). The 0002 Ti diffraction ring emanates from untransformed portions of the Ti layer. The size of the TiF₃ domains are comparable to the average Ti grain size, 37 nm, in the as-deposited films, suggesting that TiF₃ formation proceeds within individual Ti grains. The interplanar spacings and the crystal structure of TiF₃ are nearly identical to those of hexagonal Ti₂O₃ (Ref. 30) which could also have formed during TEM sample preparation. Thus, in order to conclusively identify the second phase, further characterization was carried out by XRD and XPS.

Typical XRD diffractograms obtained from 250-nm-thick Ti samples exposed to WF₆ are reproduced in Figs. 9(a) and 9(b). Thicker samples were used to reduce the relative contribution of diffracted intensity from native surface oxides (angle-resolved RBS showed that oxygen was confined to the surface of the samples), and to obtain better signal-to-noise ratios for low-intensity peaks. The Ti(0002) and (10\bar{1}0) peaks at 2\theta = 38.4° and 34.6° are the only Bragg reflections obtained from as-deposited samples, indicating an (0002) texture. Diffractograms obtained following WF₆ exposure contain additional Bragg peaks due to TiF₃ formation,
(0112) and (0224) at 2θ = 22.9° and 46.8°, and bcc W deposition, (110) at 2θ = 40.3°.

Comparisons of relative intensities of the TiF₃ peaks with tabulated powder diffraction data reveal that TiF₃ grows with a (0112) texture. Figure 9(b) shows that increasing $P_{WF₆}$ to 0.55 Torr results in an increase in the TiF₃ (0112) peak intensity with a simultaneous decrease in the Ti (1010) peak intensity. The Ti (1010) peak intensity, which was barely detectable in the as-deposited sample [Fig. 9(a)], increases abruptly for exposures at $P_{WF₆}$ > 0.55 Torr. We attribute the latter, as well as the shift in the 1010 Ti peak to higher angles, to the delamination of the Ti layer which brings the (1010) planes into Bragg alignment. An alternative explanation for the increase in the peak intensity would require the preferential growth of (1010)-oriented Ti grains at 445 °C. This is unlikely, however, since grain growth is expected to be insensitive to $P_{WF₆}$, whereas the observed change is abrupt and occurs only at high WF₆ exposures.

Figure 10(a) shows XRD diffractograms obtained in the vicinity of the Ti(0002) peak, 2θ = 38.47°, from 27-nm-
thick Ti samples exposed to WF$_6$ at different partial pressures. Raising $p_{WF_6}$ from 0 to 0.20 Torr resulted in an increase in the (0002) Ti interplanar spacing from 0.234 to 0.238 nm due to F incorporation. The Ti(0002) peak position remains constant at 37.77° 2$\theta$ with further increases in $p_{WF_6}$ indicating that the Ti layer is already saturated with F at partial pressures<0.2 Torr. Diffractograms obtained with extended counting times from WF$_6$-exposed Ti/SiO$_2$ samples show weak 0112 TiF$_3$ diffraction peaks at $2\theta$=23° (inset in Fig. 10). While the TiF$_3$ peak intensity increases when $p_{WF_6}$ is raised to 0.35 Torr, it decreases with further WF$_6$ exposure at $p_{WF_6}$=0.55 Torr, and disappears completely at 1.3 Torr.

In order to determine F depth distributions in Ti, the chemical state of Ti, and to distinguish TiF$_3$ from TiF$_{O_x}$ compounds, XPS measurements were carried out on Ti films before and after WF$_6$ exposure at 0.2 Torr. The W overlayer was removed from the WF$_6$ exposed samples by wet-chemical etching in K$_2$Fe(CN)$_6$ prior to XPS analyses. Spectra I and II in Fig. 11(a) show Ti 2$p$ XPS peaks obtained from as-deposited and WF$_6$-exposed samples, respectively. Spectra III and IV were obtained after removing the native oxide by sputter etching using 5 keV Ar$^+$ ions. The corresponding F 1$s$ spectra are shown in Fig. 11(b). The Ti 2$p_{3/2}$ binding energy for the as-deposited sample was $\approx$458.9 eV. This agrees very well with Ti 2$p_{3/2}$ peak positions obtained from commercially synthesized Ti$_2$O$_5$ and TiO$_2$. Spectrum II in Fig. 11(a) shows that the Ti 2$p_{3/2}$ binding energy for the WF$_6$-exposed sample was slightly higher at $\approx$459.4 eV. This increase in the metal binding energy results from the presence of residual amounts of electronegative F as indicated by the emergence of the F 1$s$ peak in spectrum II, Fig. 11(b).

Removal of the surface oxide in the as-deposited sample resulted in a decrease in the Ti 2$p_{3/2}$ binding energy to $\approx$454.1 eV, the expected peak position for pure Ti, as shown by spectrum III in Fig. 11(a). The sputter-etched WF$_6$-exposed sample, spectrum IV in Fig. 11(a), exhibited three overlapping Ti 2$p$ peaks with maxima at $\approx$454.1, 461.2, and 467.1 eV. This is accompanied by a significant increase in the F concentration as shown by the corresponding spectrum IV in Fig. 11(b). Comparison of experimental data with simulated spectra obtained using PHI 5000 series ESCA software showed that the Ti 2$p$ triplet arises from three distinct sets of chemical states (see Fig. 12). The main component of the highest-intensity central peak of the triplet is centered at 461.4 eV, which is identical to the Ti 2$p_{3/2}$ binding energy measured from commercially synthesized TiF$_3$ samples. The Ti 2$p_{1/2}$ peak from pure Ti, and a low intensity Ti 2$p_{3/2}$ peak at 458.2 eV arising from the presence of a small amount of Ti oxide also contribute to the central peak. The high binding energy peak at 467.1 eV is the Ti 2$p_{1/2}$ component from TiF$_3$, while the low energy peak at 454.1 eV is primarily due to the Ti 2$p_{3/2}$ component from pure Ti.

The XPS results combined with the diffraction data above conclusively demonstrate that the major nonvolatile F-containing compound formed upon exposing Ti to WF$_6$ is TiF$_3$. The overall reaction path leading to compound formation at low $p_{WF_6}$ exposures can be expressed as

$$2WF_6(g) + 4Ti(s) \rightarrow 2W(s) + 4TiF_3(s).$$

From tabulated thermochemical data,$^{31}$ the calculated Gibbs free energy change for reaction (1) at 445°C is $\Delta G = -8.7$ eV, indicating that, in the absence of kinetic barriers, the reaction will proceed to the right.
The rapid etching of Ti by WF\textsubscript{6} at $p_{\text{WF}_6} > 0.35$ Torr requires the evolution of a volatile Ti-containing compound. Since TiO\textsubscript{x}, and TiW\textsubscript{x}, and TiF\textsubscript{3} are not volatile at 445 °C,\textsuperscript{32–34} and our RBS analyses suggest the evolution of a F-containing species at high $p_{\text{WF}_6}$, the feasibility of the TiF\textsubscript{4} formation was examined. The RBS results presented in Fig. 6 show that the amounts of Ti consumed and W deposited after WF\textsubscript{6} exposure at $p_{\text{WF}_6} = 1.3$ Torr are (within 10\% accuracy) $1.45 \times 10^{17}$ and $8.25 \times 10^{16}$ atoms/cm\textsuperscript{2}, respectively. Assuming that TiF\textsubscript{3} compound formation and W deposition occur by the reduction of WF\textsubscript{6} by the Ti film, $x$ was estimated by simple mass balance to be $3.4 \pm 0.7$, which is consistent with TiF\textsubscript{4} evolution. Thus, Ti reduction of WF\textsubscript{6} at high values of $p_{\text{WF}_6}$ can be represented as

$$2\text{WF}_6(g) + 3\text{Ti}(s) \rightarrow 2\text{W}(s) + 3\text{TiF}_4(g).$$

This reaction has a thermodynamic driving force $\Delta G = -14.6$ eV at 445 °C.\textsuperscript{31}

IV. DISCUSSION

A. W deposition by Ti reduction of WF\textsubscript{6}

W deposition on Ti during WF\textsubscript{6} exposure occurs via chemisorption of impinging WF\textsubscript{6} molecules followed by a series of surface dissociation reactions. Since the precursor is F rich, the Ti surface is rapidly saturated with F. However, F diffusion into the Ti film is faster than F adsorption, exposing F-depleted Ti surfaces to the incident flux, thereby allowing further WF\textsubscript{6} reduction until a continuous W layer is formed. This is seen from our RBS results showing that the ratio of F in the Ti film to deposited W is $\approx 6$ at low exposures, indicating that essentially all F diffuses into the Ti film. This interpretation is also corroborated by the XPS depth profiling results showing a low surface F concentration and is consistent with the absence of appreciable TiF\textsubscript{4} evolution at low WF\textsubscript{6} exposures.

We propose that further W deposition is facilitated by microcracking and delamination of the initially continuous W overlayer due to residual stresses generated near the W/Ti interface at local regions of high F concentration. Development of residual stresses due to F incorporation is indicated by our XRD results showing the expansion of the hcp Ti lattice due to Ti–F solid solution formation, and a 230\% volume expansion of the primitive unit cell\textsuperscript{29,35} occurring during the Ti→TiF\textsubscript{3} transformation. Microcracks expose portions of the Ti layer with relatively low F content, promoting WF\textsubscript{6} reduction and local growth of W particles, and increasing the local F concentration. Thus, new W/Ti interfaces with higher F concentrations are created, leading to a cascaded-metallization process.
ing effect. The connection between stress-induced cracking of the W film and localized particle growth is supported by our SEM results which show enhanced particle growth around microcracks. This argument is also consistent with enhanced growth and microcracking observed at the edges of topological features which are expected to have high stress concentrations.

Our XPS results demonstrate that the presence of a thin native layer on Ti does not prevent W deposition. In fact, the oxide layer remains relatively intact even after enormous quantities, \( \approx 2.0 \times 10^{17} \) atoms/cm\(^2\), of F have penetrated through it. Thus, while the presence of a native Ti oxide may alter the reaction kinetics, it does not prevent WF\(_6\) reduction. This is supported by the results of Lee and co-workers,\(^{36} \) who have verified the feasibility of WF\(_6\)-exposed TiN/Ti samples.\(^{18} \)

B. Phase formation sequence

Our results demonstrate that the phase formation reaction path during WF\(_6\) reduction by Ti depends strongly on the amount of WF\(_6\) exposure, and provides a basis for understanding the conflicting reports of previous studies.\(^{19,20,22-24} \) At low WF\(_6\) exposures, \( p_{WF_6} < 0.2 \) Torr, F rapidly diffuses into the Ti film and forms a solid solution. F dissolved in Ti expands the hcp lattice as indicated by an increase in the Ti(0002) interplanar separation. The presence of untransformed Ti grains together with TiF\(_3\) domains as shown by our TEM results when the F/Ti ratio is <3, is consistent with the dissolution of F in Ti at low \( p_{WF_6} \) values. TiF\(_3\) formation is expected to occur by the reaction of Ti–F solid solution with incident WF\(_6\) in regions with a large population of microcracks near the W/Ti interface. As WF\(_6\) reduction proceeds and the average F concentration in the Ti film continues to increase, entire Ti–F grains are transformed into TiF\(_3\). The columnar arrangement of F between Ti atoms in the TiF\(_3\) unit cell when viewed along the (0002) zone axis, and the small atomic size of F compared with the interatomic spacings in the Ti lattice, suggest that F diffuses through interstitial sites in the (0002) textured Ti film.

High WF\(_6\) exposures, \( p_{WF_6} > 0.35 \) Torr, cause fluorination of TiF\(_3\), resulting in TiF\(_4\) evolution. This reaction path, TiF\(_4\) formation by the consumption of TiF\(_3\), is indicated by the concurrent decrease in TiF\(_3\) XRD and Ti RBS and XRD peak intensities observed in thin Ti samples exposed at \( p_{WF_6} > 0.35 \) Torr. The persistence of the Ti(0002) XRD peak until just prior to the onset of Ti etching (\( p_{WF_6} = 0.35 \) Torr) shows that a Ti–F solid solution is present even when the nominal concentration in the Ti layer is high enough to form volatile TiF\(_4\). Regions of low F concentration in the Ti film due to the local presence of an intact W overlayer with a low population of microcracks is the likely reason for the continuing presence of Ti–F solid solution at high WF\(_6\) partial pressures.

The phase formation sequence outlined above can be understood as follows. Ti–F solid solution formation is energetically favored over titanium fluoride formation when \( C_F < C_F^* \), which point the free energy of the system is reduced by compound formation. The equilibrium solubility limit of F in Ti is not known. However, we estimate the lower limit of \( C_F^* \) in our experiments (which are far from equilibrium) to be \( \approx 10 \) at. % based upon combined XRD, RBS, and SIMS analyses of WF\(_6\)-exposed TiN/Ti samples.\(^{18} \)

While both TiF\(_3\) formation and TiF\(_4\) evolution are thermodynamically feasible when \( C_F^* < C_F^\prime \), the reaction leading to TiF\(_4\) formation has a larger driving force [see Eqs. (1) and (2)] than that causing TiF\(_3\) formation. However, our results show that TiF\(_3\) formation prior to TiF\(_4\) evolution indicates that TiF\(_3\) formation—by the fluorination of Ti–F solid solution—has a lower kinetic barrier. Thus, when \( C_F^* \) is exceeded at low WF\(_6\) partial pressures, the Ti–F solid solution rapidly transforms to TiF\(_3\), while at high WF\(_6\) exposures, TiF\(_4\) evolution occurs by the fluorination of TiF\(_3\) through the reaction

\[
WF_6(g) + 6TiF_3(s) \rightarrow W(s) + 6TiF_4(g),
\]

resulting in a free energy decrease \( \Delta G = -3.1 \) eV. TiF\(_4\) evolution can also occur by this reaction pathway at low \( p_{WF_6} \) when WF\(_6\) reacts with TiF\(_3\) formed at local areas on the Ti surface. This explains the observation that small amounts of Ti are removed even at \( p_{WF_6} < 0.35 \) Torr.

C. Reaction mechanism and W morphology

The disappearance of the entire Ti film, despite the presence of a 120-nm-thick continuous W overlayer, can be understood based upon a phenomenological model illustrated schematically in Fig. 13. At low \( p_{WF_6} \), TiF\(_3\) formation in local areas near the W/Ti interface causes microcracking and delamination of the W overlayer. The impinging WF\(_6\) molecules are reduced by the freshly exposed areas of Ti, leading to enhanced growth of W particles. With increasing WF\(_6\) exposure, entire Ti grains are transformed to TiF\(_3\). The large stresses developed at the Ti/SiO\(_2\) interface due to TiF\(_3\) formation, in addition to the displacement of the Ti–O and Ti–Si bonds (essential to maintain good adhesion) by Ti–F bonds weaken the interface resulting in local delamination of the Ti film. Elongated microcracks across the film and delaminated areas both provide access for WF\(_6\) to penetrate the W film and attack the unreacted portions of the delaminated Ti film. Thus, W deposition proceeds from below as well (see Fig. 13). When most of the Ti layer has been converted to TiF\(_3\), further WF\(_6\) exposure results in the evolution of TiF\(_4\) through the microcracks in the W film until the entire Ti layer is consumed, leaving behind a free standing W film which has extremely poor adhesion to the SiO\(_2\) substrate.

V. CONCLUSIONS

WF\(_6\) exposure to Ti leads to reduction and W deposition as F rapidly penetrates the Ti layer even when a Ti oxide is present on the surface. The primary Ti fluoride phase formed is determined by the WF\(_6\) dose. At low WF\(_6\) partial pressures, a Ti–F solid solution and a nonvolatile TiF\(_3\) compound are formed. The large stresses generated by TiF\(_3\) formation result in the formation of microcracks in the W film and delamination of the Ti layer at the Ti/SiO\(_2\) interface. At high partial pressures, WF\(_6\) continues to attack the underlying—
leaving behind a W film with extremely poor adhesion to the SiO₂ substrate.

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