Surface chemistry of the WF_6-based chemical vapor deposition of tungsten

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This paper is an overview of work at the IBM Thomas J. Watson Research Center on chemical aspects of the WF_6-based chemical vapor deposition of tungsten. The focus is on two deposition processes. In the first process, tungsten deposition occurs through the chemical reduction of WF_6 by a silicon substrate. The thickness of the tungsten film thus grown is limited by the transport of silicon through the deposited film. In the second process, deposition occurs in a WF_6–silane mixture by the following reactions: reduction of adsorbed WF_6 by a surface layer of silicon to form tungsten, and the concurrent dehydrogenation of the adsorbed silane to replenish the silicon. This process permits the deposition of tungsten on any substrate, provided the initial reaction of the substrate with the WF_6–silane mixture can provide a tungsten or silicon "seed" layer to initiate the reaction cycle. Furthermore, the process is not limited by tungsten film thickness and hence permits the deposition of relatively thick films. Although surface selectivity is possible with regard to materials such as high-quality SiO_2, on which such a seed layer cannot be formed, the selectivity is adversely affected by the presence of particulates.

Introduction

The chemical vapor deposition (CVD) of tungsten using tungsten hexafluoride (WF_6) provides a relatively low-temperature, low-pressure process for use in VLSI-level metallization [1–6]. Tungsten has all the favorable characteristics of a refractory metal, and a relatively low bulk resistivity: 5.3 $\mu\Omega$-cm. Films having a resistivity of about 15 $\mu\Omega$-cm can be deposited by CVD. The use of CVD avoids the nonuniform coverage over stepped structures that is inherent in physical deposition. Structures (e.g., via holes) with large aspect ratios can thus be filled. Basically, the chemistry of the processes described here is the reduction of WF_6 to tungsten, and the removal of fluorine through the formation of a volatile reaction product. The first process involves the reduction of WF_6 by silicon, and the second the reduction of WF_6 by silane (SiH_4).

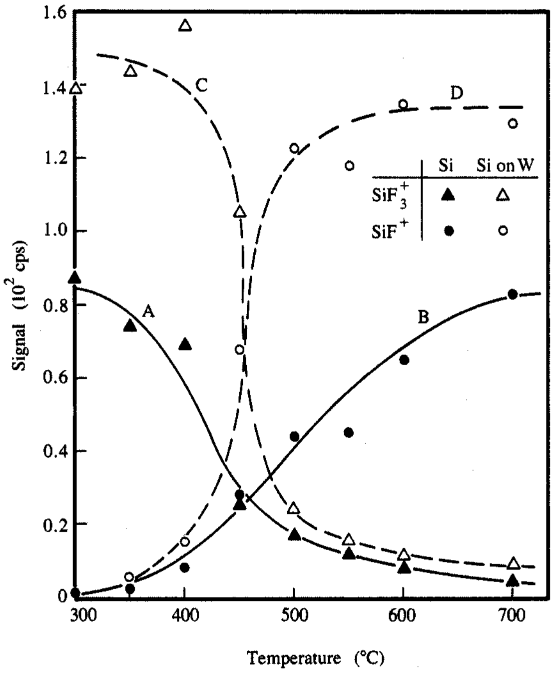

Figure 1

Dependence on temperature of SiF_4 (SiF_3^+) and SiF_2 (SiF^+) mass spectrometer signals from a Si(100) surface (Curves A and B), and a W film containing a Si surface layer (curves C and D) during reaction with WF_6. From [7], reproduced with permission.

An important feature of the WF_6-based CVD of tungsten is that the deposition is surface-selective. For example, tungsten can be selectively deposited on Si, but not on (high-quality) SiO_2. This indicates that the chemistry of the deposition is dominated by a surface reaction. The selectivity arises from the differing reactivity of WF_6 on surfaces of different chemical composition. Hence, the most direct information on the deposition chemistry has been obtained from surface-related experiments.

Such experiments have been performed by the authors and others using ultrahigh-vacuum (UHV) systems with base pressures in the vicinity of 2×10^{-10} torr. Under such conditions, gas-phase reaction can be neglected, and gas-phase contamination can be minimized. Photoemission spectroscopy, either via X-ray radiation (XPS) [7–12] or synchrotron radiation [13–15], has been used to identify the chemical species involved and their chemical states on sample surfaces. Such information is obtained from the binding energies (b.e.) of the core levels of the atoms. The gaseous reaction products are best monitored by mass spectrometry. Temperature-programmed desorption [10, 16, 17] provides qualitative information on the evolution of reaction products at various temperatures as samples are heated slowly to a high temperature. The combination of pulsed molecular-beam and time-resolved mass spectrometry [7, 9, 18] allows relevant reaction pathways and kinetics to be studied at a constant sample temperature. Auger electron spectroscopy and low-energy electron diffraction are also useful. All of these techniques have been used for the study of the WF_6 reaction, and experimental details have been reported in the references cited.

Deposition by the reduction of WF_6 by Si

- *Reaction of WF_6 on silicon*

Because of the relevance of tungsten deposition to the silicon microelectronics technology, most of our studies have focused on the reaction of WF_6 with silicon. Condensation of WF_6 occurs on silicon without dissociation at 120 K and below [16, 17] but reacts dissociatively at room temperature and above [7, 14]. Yu et al. [7, 18] have reported that WF_6 has a very high initial (i.e., low-coverage) sticking coefficient, 0.3, on Si(100) from 200–700°C. The gas chemisorbs dissociatively on both Si(100) [7] and Si(111) [14]. High-resolution photoemission experiments by Yarmoff and McFeely [14] have revealed the formation of a range of fluorosilyl compounds SiF_x ($x = 1, 2, 3$) on the Si(111) surface when the surface is saturated with WF_6 at room temperature. The behavior of WF_6 on Si(100) is qualitatively similar [7]. The saturation coverage on Si(100) has been estimated to be about $1.5 \times 10^{14}/cm^2$, which is much less than the number of first-layer silicon atoms on Si(100) ($6.8 \times 10^{14}/cm^2$). This is because every WF_6 molecule contains six fluorine atoms, and the reaction stops when all of the upper-layer silicon atoms have reacted with fluorine atoms.

In order to sustain the tungsten deposition, the SiF_x species must be removed at elevated temperatures as volatile products. By using mass spectrometry, the following reaction pathways have been identified by Yu et al. [7, 18]:

$$2WF_6 + 3Si \rightarrow 2W + 3SiF_4\uparrow, \tag{1}$$

$$WF_6 + 3Si \rightarrow W + 3SiF_2\uparrow. \tag{2}$$

The branching between the two reaction pathways is very temperature-dependent. Curves A and B in **Figure 1** show the production of SiF_4 (SiF_3^+) and SiF_2 (SiF^+) on a Si(100) surface at various reaction temperatures. At 300°C, reaction pathway (1) dominates and SiF_4 is the major reaction product. At temperatures greater than 400°C, reaction pathway (2) becomes increasingly important, and at 700°C, SiF_2 is the major reaction product. Since the

CVD of tungsten is usually carried out at a temperature around 400°C, reaction pathway (1) is the significant one. The time evolution of both reaction products proceeds through a fast "channel" through which the product molecules are desorbed immediately after the reaction of the WF_6 molecules with the surface. The short residence time suggests that the fluorine atoms in the reaction products are provided directly by the WF_6 molecules, and that the diffusion of fluorine on the surface is not involved. In addition, the evolution proceeds through a slower channel which depends on the surface diffusion of fluorine to form the reaction products. At high fluorine coverage, the slow (diffusion) channel dominates [18].

Mechanisms of film growth

Once a monolayer of tungsten is deposited, the silicon-reduction reaction would be expected to stop in the absence of a mechanism to supply silicon to the tungsten surface. Yarmoff and McFeely [14] and Yu et al. [7] have independently identified that the segregation of silicon from the silicon substrate through the tungsten monolayer to its surface is the important mechanism for sustaining the supply of silicon. The reaction of WF_6 with silicon atoms thus segregated on the tungsten surface has been studied by photoemission and mass spectrometry [7, 18]. It was found that the reaction pathways for such silicon atoms are identical to those of the surface of the silicon substrate. Curves C and D in Figure 1 show the production of SiF_4 (SiF_3^+) and SiF_2 (SiF^+) on a W film containing a Si surface layer. The curves indicate that the temperature dependence of the branching is qualitatively similar to that for the silicon surface (curves A and B). The difference between these two sets of curves can be accounted for by a higher sticking coefficient (0.5) for the WF_6 in the case of the silicon atoms segregated on the tungsten.

The need for silicon diffusion affects the film growth rate. Green et al. [19] have reported that the initial tungsten deposition rate is very high. The rate drops off rapidly with increasing film thickness, causing the film to reach a "self-limiting" thickness that is temperature-dependent. The behavior can be simply explained by the rapid decrease in the silicon diffusion flux as the tungsten film thickness increases. The empirical activation energy derived from the temperature dependence of the "self-limiting" film thickness deposited under identical CVD growth conditions in an ultrahigh-vacuum system was found to be about 0.48 eV [8], which is appreciably lower than the diffusion activation barrier (3.0 eV [20]) for silicon diffusion in tungsten. This could be due to the sensitivity of the diffusion to the nature of the tungsten/silicon interface, the presence of tungsten grain boundaries, and/or the presence of contamination. For example, very different temperature dependences of the "self-limiting" thickness have been reported for films grown in nonultrahigh-vacuum systems in which interfacial cleanliness and contaminations were not well controlled [19].

Film growth by the reduction of WF_6 by silane

General characteristics

Tungsten deposition by the previous process consumes silicon from the silicon substrate and causes a reduction of the volume of the substrate. The required transport of silicon through the tungsten film also places a practical upper limit on the thickness of the tungsten film. Replacing silicon with another reducing agent can alleviate most of these problems. Hydrogen has frequently been used as a reducing agent [6]. However, its use gives a growth rate of only about 100 Å/min at 300°C. Recently it has been found that silane (SiH_4) is a more effective reducing agent, providing deposition rates up to 5000 Å/min at 300°C [21]. Higher silanes (Si_nH_{2n+2}) can be effective [21] at even lower temperatures. For the remainder of this paper, we focus on the use of silane for this purpose, at temperatures around 300°C.

If we consider only mass balance, and assume that the reaction products after the introduction of silane are SiH_4, H_2, and HF, there can be a very large number of reaction pathways, viz.,

$$x\mathrm{SiH}_4 + y\mathrm{WF}_6 \rightarrow y\mathrm{W} + x\mathrm{SiF}_4 + (6y - 4x)\mathrm{HF} + (4x - 3y)\mathrm{H}_2, \qquad (3)$$

where $4x \geq 3y \geq 2x$. All of these pathways are exothermic, releasing $134.7(x/y) - 22.7$ kcal/mol of tungsten deposited in the solid state. Observations by mass spectrometry have shown that hydrogen production is the major reaction pathway [9] in this solid-surface-mediated reaction. Despite the implications of the mass balance equation, WF_6 and silane do not react directly. The reaction is mediated by the substrate surface. In essence, the silicon on the substrate reduces the WF_6, resulting in the deposition of tungsten; and concurrently the silane dehydrogenates on the tungsten surface, supplying the required silicon. The tungsten deposition can be viewed as the net result of the deposition of silicon and tungsten, and the removal of the silicon as SiF_4. The supporting evidence for these reactions has been obtained by studying the reaction of the WF_6/silane mixture with silicon and tungsten surfaces [9].

Initial reaction on a silicon surface

The Si(100) surface was used to study this reaction [9]. The reaction starts with the chemisorption of WF_6 and SiH_4 on the Si(100) surface. While the sticking coefficient WF_6 is 0.3 on the silicon surface, that of silane is negligible: <0.01 [22]. This implies that despite the introduction of silane, the initial reaction is the reduction of WF_6 by the silicon atoms on the silicon substrate.

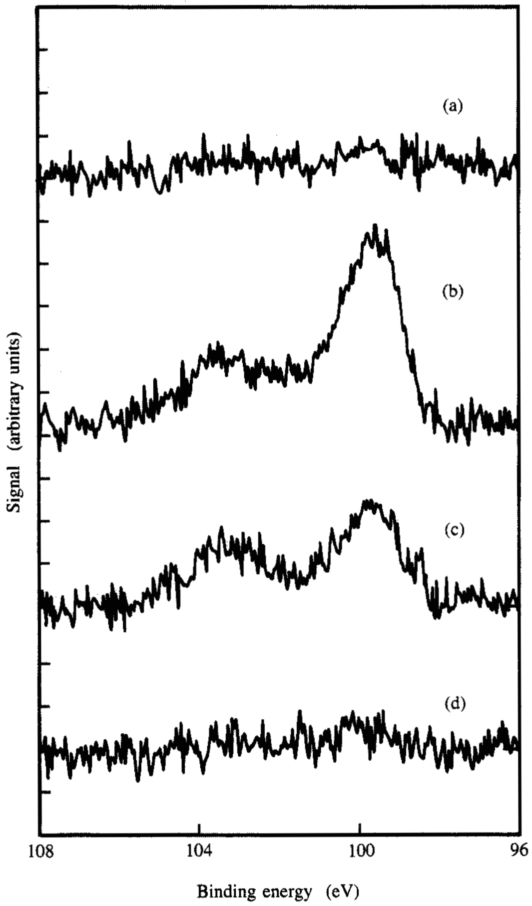

Figure 2

Silicon 2p XPS spectra: (a) from initial fluorinated tungsten surface; (b) after exposure to 1 × 10^{-6} torr of SiH_4 at 300°C for 30 s; (c) after exposure to 1 × 10^{-4} torr of WF_6 at 300°C for 20 s; and (d) after exposure to 1 × 10^{-4} torr of WF_6 at 300°C for a total of 80 s. From [9], reproduced with permission.

- *Initial reaction on a tungsten surface*

Silane plays an important role after an initial layer of tungsten has been formed. This has been studied by XPS [9]. Interestingly, WF_6 is readily adsorbed on clean tungsten surfaces [8]. Tungsten deposited in a WF_6 ambient does not result in a pure tungsten surface. Using XPS, we have detected the presence of close to a monolayer of fluorine, which can be removed only at temperatures close to 500°C. Silane reacts readily on such a fluorinated surface. **Figures 2** and **3** show the Si 2p and F 1s XPS spectra during the reaction of silane with the fluorinated surface. Spectra 2(a) and 3(a) were from a fluorinated tungsten surface prior to silane exposure, showing the absence of silicon and the presence of a monolayer of fluorine; the F 1s peak was located at 684.1 eV, which is characteristic of fluorine on a tungsten surface. Molecular beam/mass spectrometry studies [9] have shown that silane reacts with fluorinated tungsten surfaces to produce H_2 and SiF_4 at temperatures around 300°C. The production of HF is important only above 600°C. Upon exposure of the fluorinated tungsten surface to 1 × 10^{-6} torr of silane at 300°C for 30 s, the Si 2p XPS spectrum [as depicted by 2(b)] showed multiple peaks, indicating the presence of both unreacted silicon and SiF_x. The most abundant silicon subfluoride formed was SiF_3, in addition to the SiF_4 that left the surface. Aside from the reduction of the F 1s peak due to the evolution of SiF_4, the F 1s peak [spectrum 3(b)] was shifted to 686.5 eV because the fluorine atoms were bonded to the silicon instead of to the tungsten. With silicon atoms deposited on the surface and all fluorine atoms bonded to silicon, the surface became inert to SiH_4.

With silicon residing on the tungsten surface, WF_6 molecules could react again through the silicon reduction reaction, leading to the deposition of additional tungsten. This is clearly shown by spectra 2(c) and 3(c), for which the silicon-covered surface was exposed to 1 × 10^{-4} torr of WF_6 for 20 s at 300°C. The surface silicon was depleted by the removal of SiF_4, the reaction product; the F 1s spectrum again showed a component at 684.1 eV which was due to the bonding of fluorine to tungsten. Exposure of the surface to 1 × 10^{-4} torr of WF_6 at 300°C for 80 more seconds practically eliminated all of the silicon atoms, and the F 1s peak was restored to 684.1 eV. This completed one reaction cycle.

- *Film growth*

The reaction mechanisms discussed above result in some important growth characteristics. The original substrate surface has a minimal effect on the chemistry of the tungsten deposition once the deposition reaction is initiated. A tungsten or silicon seed layer is all that is required to initiate the tungsten deposition. An important corollary is that tungsten can be deposited on any substrate provided that the reaction of the WF_6/silane mixture with the initial substrate surface can create the necessary tungsten or silicon seed layer. The initial reaction also determines the selectivity of the tungsten deposition, potentially broadening the applicability of the process.

The initial rate of tungsten deposition is determined by the rate of the reaction that creates the necessary tungsten or silicon seed layer. This can appear as an "incubation" period before the normal tungsten growth can begin. Once the seed layer is in place, the tungsten growth rate is independent of the original substrate, and is completely determined by the deposition reaction discussed above, allowing continued deposition.

In the mass balance equation (3), silicon is assumed to be removed completely as SiF_4. However, we have found that the deposition of silicon from silane onto the fluorinated tungsten surface does not depend on the WF_6 ambient. The amount of silicon deposited can exceed what is necessary for the deposition of the tungsten film. Hence, with the proper combination of silane concentration and temperature, excess silicon can be embedded in the tungsten film, leading to the formation of tungsten silicide at appropriate temperatures [23].

Deposition of tungsten onto various substrates

As discussed above, the initial reaction of the substrate with the WF_6/silane mixture determines whether a silicon or tungsten seed layer can be deposited to initiate the tungsten growth reaction. Once the seed layer is in place, the tungsten deposition reaction is independent of substrate type. Hence, we need only examine the initial reaction of the WF_6/silane mixture with the substrate to determine whether the deposition of tungsten is feasible.

1. Deposition onto silicon and silicide substrates

The silicon atoms on silicon [7] or silicide substrates [10] naturally form a seed layer. In either case, the reaction that initiates the deposition is the reduction of WF_6 by silicon.

2. Deposition onto an aluminum substrate

Tungsten can be deposited on aluminum at a substrate temperature of about 350°C [24, 25]. As in the case of silicon, aluminum does not react with silane readily at 350°C, but WF_6 reacts strongly with it even at room temperature, forming a range of aluminum fluorides. This was indicated by Al 2p XPS spectra, which showed the presence of subfluorides and the predominant formation of AlF_3 [10]. In contrast to SiF_4, AlF_3 is not volatile at 350°C: Fluorine is removed through the evolution of AlF_2, as identified by mass spectrometry [10, 11]. Upon exposure of a clean Al surface to WF_6 at room temperature, followed by ramping the temperature at a rate of about 1.2°C/s, desorption of AlF_2 was observed, but no AlF_3 was detected. **Figure 4** shows desorption data after exposure at room temperature to (a) 2 L, (b) 10 L, and (c, d) 100 L of WF_6. The peak of the AlF_2 desorption shifted to higher temperatures with an increase in WF_6 dosage, indicating that the desorption was not first-order. Analysis by XPS showed that depletion of AlF_3 occurred during the annealing, indicating that the desorbed AlF_2 originated from the reduction of AlF_3 to AlF_2 by surrounding, unreacted aluminum; this showed that the AlF_2 desorption was not first-order. The AlF^+ signal was found to have a temperature dependence which was identical to that of the AlF_2^+, showing that the AlF^+ arose from the cracking of AlF_2 in the mass spectrometer ionizer. The ability of AlF_3 to be converted to the volatile AlF_2 is crucial in providing a good contact resistance between aluminum and tungsten. The use of a higher processing temperature should have a positive effect on minimizing this resistance.

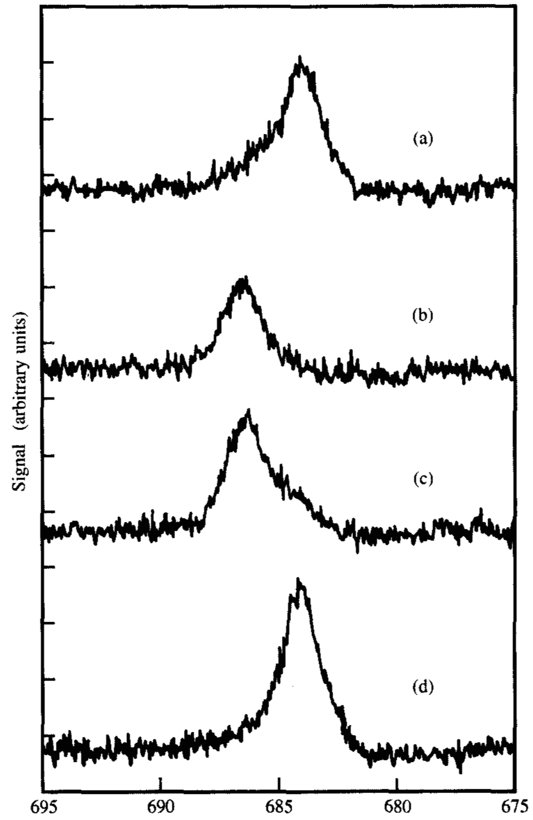

Figure 3

Fluorine 1s XPS spectra: (a) from initial fluorinated tungsten surface; (b) after exposure to 1×10^{-6} torr of SiH_4 at 300°C for 30 s; (c) after exposure to 1×10^{-4} torr of WF_6 at 300°C for 20 s; and (d) after exposure to 1×10^{-4} torr of WF_6 at 300°C for a total of 80 s. From [9], reproduced with permission.

The initial reaction pathway can hence be summarized as follows:

$$WF_6 + 2Al \rightarrow W + AlF_3,$$

$$2AlF_3 + Al \rightarrow 3AlF_2\uparrow . \qquad (4)$$

The resulting tungsten seed layer can be used to initiate the deposition process.

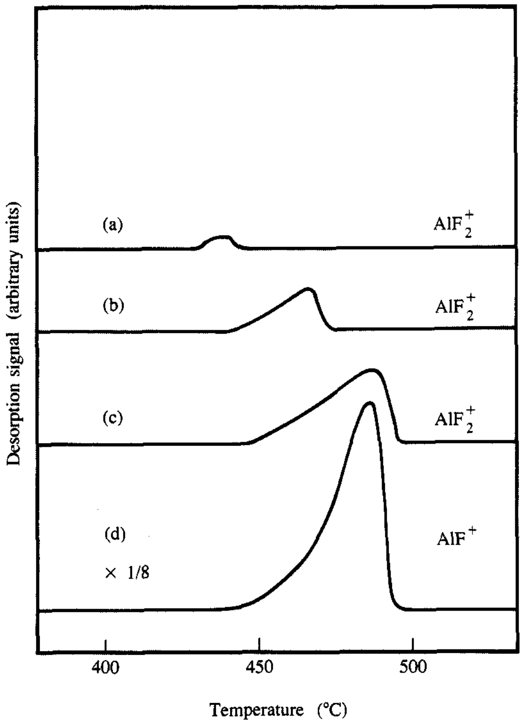

Figure 4

Thermal desorption of AlF_2^+ after exposure at room temperature of an aluminum substrate to (a) 2 L, (b) 10 L, (c) 100 L of WF_6. Curve (d) shows corresponding desorption of AlF^+ after exposure to 100 L of WF_6. From [10], reproduced with permission.

3. *Deposition onto a TiN substrate*

The CVD of tungsten on TiN has received much attention recently [26, 27]. The latter forms a conducting fluorine barrier for $TiSi_2$ and provides a good contact resistance to an overlying tungsten film. Either WF_6 or silane can be reacted with TiN to deposit a seed layer for tungsten deposition [10, 11]. We first discuss reaction with WF_6.

Figure 5 shows Ti 2p, N 1s, W 4d, and F 1s XPS spectra after various surface treatments. The Ti 2p and N 1s spectra from surfaces of Ti and TiN (formed *in situ* on Ti) are indicated, respectively, by (a) and (b). The Ti 2p spectrum is a composite of two components: the $2p_{3/2}$ and $2p_{1/2}$ spectra. Our discussion refers to the $2p_{3/2}$ component, for which the b.e. is lower. After the *in situ* formation of the TiN, the Ti $2p_{3/2}$ component contained a shoulder corresponding to a binding energy of about 456.6 eV, associated with TiN. The corresponding N 1s XPS spectrum (b) peaked at 397.2 eV. It was found that WF_6 adsorbed readily even at room temperature on TiN, but that the WF_6 molecules did not fully dissociate. The XPS spectrum (c) obtained after exposure to 1×10^{-6} torr WF_6 for 100 s (100 L) at room temperature is shown. The F 1s XPS spectrum peaks at 684.7 eV. Its magnitude suggests about a monolayer of coverage. There was no evidence for the formation of titanium fluorides. By comparison, spectrum (e) was obtained after a clean Ti surface was exposed to 100 L of WF_6 at room temperature. The b.e. of the Ti 2p peaks (461.2 eV) was shifted higher by about 7.3 eV, which is attributed to the formation of TiF_3 on the surface. The associated F 1s peak has a b.e. of 686.0 eV. When the TiN surface with the WF_6 layer adsorbed at room temperature was heated slowly, the evolution of TiF_4 and N_2 was observed, starting at about 65°C and peaking at about 85°C. This is in accordance with the high volatility of TiF_4, which has a boiling point of 284°C. Spectrum (d) was obtained after heating to 300°C for five minutes. All of the WF_6 molecules dissociated, and the deposited tungsten was in metallic form, with the binding energy of the W $4d_{5/2}$ shifted to 244.0 eV. The amount of fluorine was depleted, and there was a reduction in the magnitude of the Ti 2p 456.6 eV (TiN) shoulder. Thus, at 65°C and above, the upper layer of the TiN substrate was decomposed by the WF_6, and TiF_4 was formed. The excess nitrogen was released as N_2.

Thus, the tungsten seed layer can be deposited with WF_6. The TiN is not very reactive, and the TiF_4 is formed only at temperatures at which TiF_4 desorption is rapid. This prevents the accumulation of TiF_4 at the W/TiN interface, which would increase contact resistance. The reaction can be summarized as follows:

$$4WF_6 + 6TiN \rightarrow 4W + 6TiF_4\uparrow + 3N_2\uparrow . \qquad (5)$$

Use can also be made of SiH_4 to decompose TiN, forming silicon nitride. **Figure 6** shows the Ti 2p and Si 2p spectra obtained after various SiH_4 exposures. The Ti 2p spectrum of the starting TiN surface grown on Ti is shown as (a). A dosage of 50 L of silane at 300°C caused deposition of about 9×10^{13} silicon atoms/cm^2 on the surface. The Si 2p portion of (b) shows both unreacted silicon (b.e. = 99.3 eV) and a broad peak at a b.e. of about 101.5 eV, which is indicative of the formation of silicon nitride. The amount of silicon nitride formed was less than a quarter of a monolayer. The Ti 2p portion of (b) shows a depletion of the TiN shoulder at a b.e. of 456.6 eV. The amount of unreacted silicon, interestingly, increased with silane exposure. Spectrum (c) was obtained after a 5000-L exposure at 300°C. The silicon coverage was about 4×10^{14}/cm^2 and contained a large unreacted component. Comparatively, the silicon nitride component increased slightly. We found that the metallic titanium formed during the reduction of the TiN has a catalytic effect on the decomposition of silane. This was confirmed by exposing a clean Ti surface to 100 L of silane at 300°C. The surface was found to be covered with a monolayer of silicon after

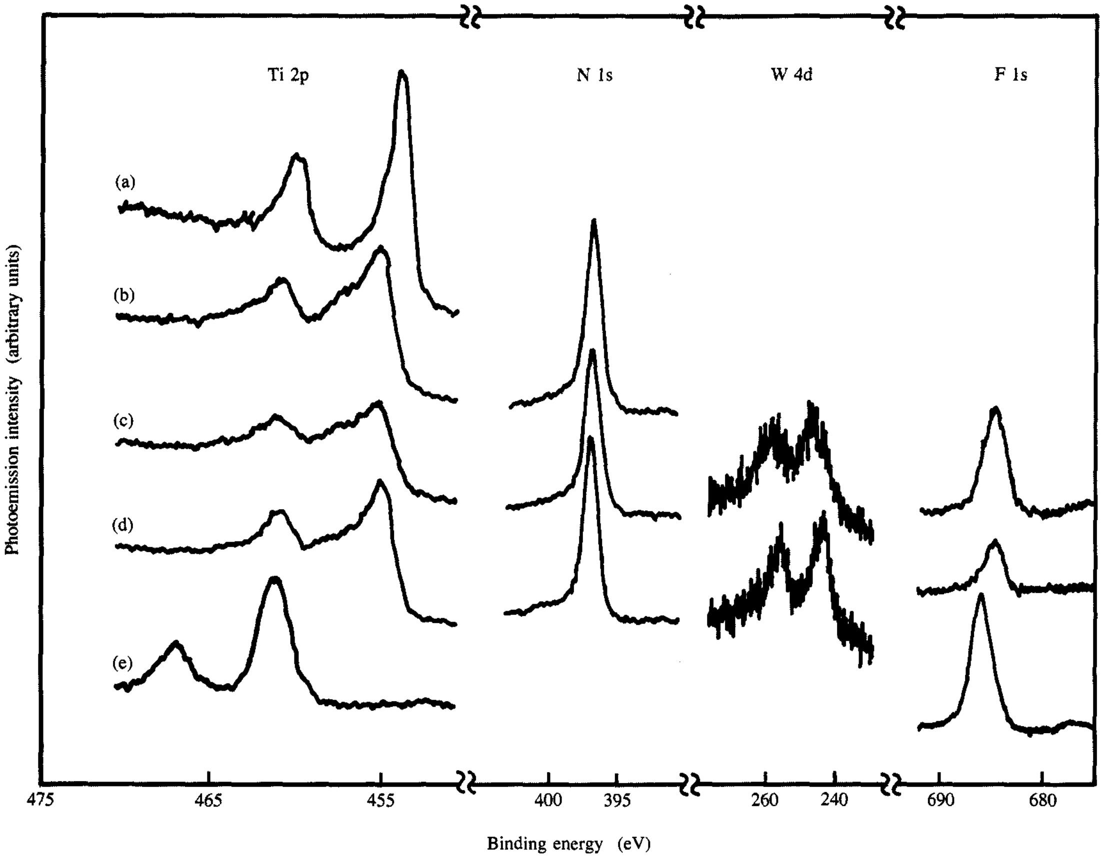

Figure 5

Ti 2p, N 1s, W 4d, and F 1s XPS spectra for (a) clean Ti surface, (b) TiN surface, (c) TiN surface exposed to 100 L of WF_6 at room temperature, (d) TiN surface of (c) annealed at 300°C for five minutes, and (e) clean Ti surface exposed to 100 L of WF_6 at room temperature. From [10], reproduced with permission.

the exposure. The initial reaction can be summarized as follows:

$$4TiN + 3SiH_4 \rightarrow 4Ti + Si_3N_4 + 6H_2\uparrow,$$

$$SiH_4 \xrightarrow{Ti} Si + 2H_2\uparrow. \qquad (6)$$

Since the TiN surface reacts with both WF_6 and silane, the details of the reaction that forms the seed layer would depend either on the sequence by which the reactants are introduced into the reactor, or their kinetics if admitted simultaneously.

Surface selectivity

One attractive feature of the WF_6-based tungsten CVD process is its potential surface selectivity. The selectivity is a manifestation of the different reactivities of various surfaces toward WF_6 and WF_6/silane mixtures. For example, the absence of deposition on SiO_2 is expected, because WF_6 should not react with SiO_2. However, in practice selectivity is frequently found to depend on the quality of the SiO_2 that is used and on other factors.

Yarmoff and McFeely have found that silicon suboxides react with WF_6 [14, 15]. Thus, tungsten can be deposited on silicon wafers that have undergone only HF cleaning and have been transported in air. Such handling leaves a thin layer of oxide and suboxide on the wafer surface. Creighton and Rogers [12, 28] have identified a pathway by which tungsten can be transported to an SiO_2 surface. According to their observations, the reaction of WF_6 with a hot (≈600°C) metallic tungsten surface (e.g., the tungsten film surface s_1) produces volatile WF_5 that can be adsorbed by a SiO_2 surface (s_2) through vapor-phase transport. Disproportionation of this tungsten subfluoride on a hot

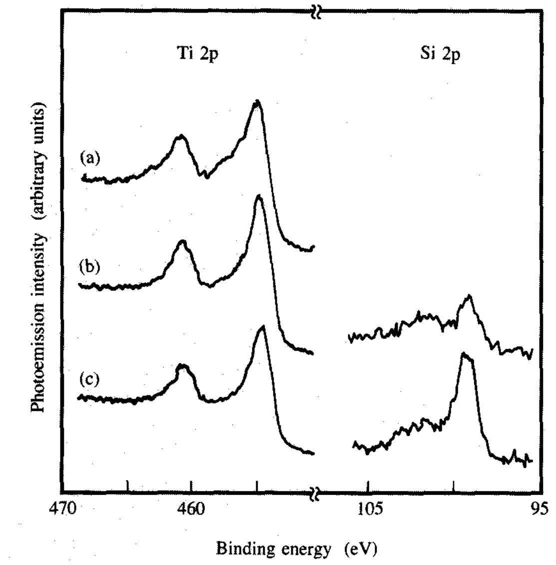

Figure 6

Ti 2p and Si 2p XPS spectra of (a) TiN surface, (b) TiN surface exposed to 50 L of silane at 300°C, and (c) TiN surface exposed to 5000 L of silane at 300°C. From [10], reproduced with permission.

SiO_2 surface produces WF_4 and finally tungsten. The relevant reactions are

$$5WF_6(g) + W(s_1) \rightarrow 6WF_5(g),$$

$$6WF_5(g) \rightarrow 6WF_5(s_2),$$

$$6WF_5(s_2) \rightarrow 3WF_4(s_2) + 3WF_6(g),$$

$$3WF_4(s_2) \rightarrow 2WF_6(g) + W(s_2). \qquad (7)$$

The deposited tungsten can further catalyze the (hydrogen) reduction of WF_6 if hydrogen is used as the carrier gas. The loss of selectivity is particularly critical for the WF_6/silane deposition reaction. The presence of particulates of tungsten, silicon, or other metals (generated by any means in the deposition chamber) that might react with WF_6/silane to deposit W or Si on the SiO_2 surface could thus cause the rapid loss of selectivity.

Summary

The reactions involved in the deposition of tungsten by WF_6-based CVD are surface-mediated. Tungsten can be deposited through the chemical reduction of WF_6 by silicon. The WF_6 reacts with the silicon to form the volatile products SiF_2 and SiF_4. The production of SiF_4 is the dominating pathway at deposition temperatures. If deposition takes place on a silicon substrate, film thickness is limited by the transport of silicon through the deposited tungsten film. This can be avoided if silane is used as the reducing agent, in a mixture with WF_6. Deposition can be initiated on any substrate provided that the initial reactions with the WF_6/silane mixture can produce a tungsten or silicon seed layer. Deposition can then continue by the following concurrent reactions: the reaction of adsorbed WF_6 with the silicon seed layer or surface silicon layer to deposit tungsten and release SiF_4, and the reaction of adsorbed silane with the deposited tungsten to replenish the consumed silicon. Although surface selectivity is possible for some materials, two drawbacks of the selectivity are its sensitivity to substrate stoichiometry when an SiO_2 substrate is used, and its sensitivity to the presence of particulates.

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