metal-containing materials having optimal properties for use in high resolution lithography.

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The Formation and Structure of CVD W Films Produced by the Si Reduction of WF_6

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ABSTRACT

In this paper, we present data on the formation and structure of CVD W films deposited by the Si reduction of WF_6. Although the great majority of CVD W films deposited for IC applications are ostensibly deposited by H_2 reduction, the Si reduction of WF_6 always occurs first, even in the presence of copious amounts of H_2. Therefore, it is the Si reduction reaction that determines the nature of W/Si interface, and, in turn, such important properties as contact resistance and leakage current. We have found that Si reduced W films deposited between 210° and 700°C are porous and discontinuous, and are probably not effective barriers to the further diffusion of WF_6. The discontinuous structure of the films provides a simple mechanism for the growth of thick W films by Si reduction; such thick films have been observed with increasing frequency as of late and have been enigmatic, because the reaction between WF_6 and Si was thought to be self-limiting. An unusual temperature dependence of W film growth is reported. Films deposited below 310°C self-limit at about 0.3×10^{17} atom/cm^2 coverage (~60Å of full dense W). In the temperature range 320°-450°C, film coverages up to 6.1×10^{17} atom/cm^2 (~950Å, at 340°C), are observed. In the higher temperature range, 500°-700°C, film coverages of about 1.5×10^{17} atom/cm^2 (200Å) are observed. The temperature dependence and the self-limiting behavior of film growth (regardless of the ultimate film thickness at which the film self-limits), are believed to be controlled by some surface-catalyzed reaction. Thus, the temperature dependence of the sticking coefficient of a reactive intermediate probably controls the reaction. This kind of model has the potential to explain why minor changes in the Si surface due to cleaning variations, for example, can result in radically different W film growth behavior.

The interest in chemical vapor deposition (CVD) of W films for a variety of integrated circuit (IC) metallization applications has increased steadily in the past five years. While most papers are concerned with the application of selective CVD W as a diffusion barrier between Al and Si at source/drain areas (1-4), other CVD W applications, *i.e.*, as an interconnect, are also gaining popularity (5, 6). Much of the latest work in the CVD W field is published in the proceedings of the 1984 and 1985 Albuquerque (Sandia) meetings on CVD refractory metals (7).

The chemical vapor deposition of W on Si, using WF_6 as the source, can involve two reactions. The first reaction, the Si reduction of WF_6, also known as the displacement reaction, involves consumption of Si

$$2WF_6 + 3Si \rightarrow 2W + 3SiF_4 \uparrow \qquad [1]$$

For every angstrom of W produced, approximately two angstroms of Si are consumed (3). Even when hydrogen is present (the H_2 reduction of WF_6 will be described next), this reaction will always occur first. The Si reduction of WF_6 can be prevented through the use of excess SiF_4 in the reactor (8), although it is not possible to eliminate Si reduction entirely without poisoning the H_2 reduction reaction. Judicious use of SiF_4, however, can minimize the erosion of Si due to Si reduction.

When SiF_4 is used, the displacement reaction usually stops once W films of about 100-200Å have formed, ostensibly due to the lack of contact between WF_6 and Si. Thicker W films can be grown on the Si-reduced W film by H_2 reduction of WF_6 according to a second reaction

$$WF_6 + 3H_2 \rightarrow W + 6HF \uparrow \qquad [2]$$

It is believed that the rate-limiting step in this reaction is the dissociation of H_2 into atomic hydrogen (9), which is probably catalyzed by the freshly deposited displaced W film. W films of unlimited thickness can be deposited by H_2 reduction.

Although the great majority of CVD W films deposited for IC applications are deposited by H_2 reduction, it is important to emphasize that even in the presence of copious amounts of H_2 (typical flows for selective CVD W film deposition are 2000 sccm H_2, 10 sccm WF_6), the dis-

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placement reaction, Eq. [1], will always take place first. This fact is dictated by the higher free energy of reaction [1] as compared to reaction [2] (−147 *vs* −15 kcal/mol of W at 327°C), and can readily be verified by selectively etching the W from source/drain windows and observing the erosion of the Si. Therefore, it is the Si reduction reaction, and not the H_2 reduction reaction, that determines the nature of the W/Si interface. In turn, this interface will determine such important device characteristics as contact resistance and leakage current, and such physical characteristics as interfacial cleanliness and silicide formation kinetics. Thus, the purpose of this paper is to exclusively study the nature of the displacement reaction, and the structure and properties of the resultant W films.

Background

A previous paper (10) reported on studies of Si-reduced W films as a function of growth temperature and crystal perfection. Figure 1 illustrates the observed temperature dependence of W film growth. The unusual temperature dependence suggests that kinetic limitations, as opposed to nucleation limitations, influence growth, because even at very low temperatures, *e.g.*, 210°-290°C, W films can nucleate, although they become self-limiting at thicknesses of less than 100Å. (Assuming full density of W, 10^{17} atom/cm^2 coverage equals 159.3Å of W.)

Other researchers have observed similar temperature dependences of W growth, as is shown in Fig. 2. The data of Fig. 1 is shown for comparison, replotted in terms of thickness, assuming full W density. Tracy (11) sees a peak in W growth at about the same temperature as the present data, 350°C. Tracy's cleaning and related processing techniques are the same as in this paper, although the deposition time is only 1 min. Itoh's data (12), generated using an unreported cleaning technique, but a protected (N_2) wafer introduction technique, reveals a strong growth peak, but at 450°C instead of the 350°C observed here and by Tracy (11). On the other hand, Broadbent's data (13), generated on samples that were introduced into a cold furnace and then heated under vacuum, show almost no temperature dependence. Thin films are always observed. They note, however, (14), that introduction into a hot ($T > 300$°C) furnace under air ambient results in thicker W films.

With the exception of Itoh's data (12), whose film thickness measurement technique is unknown, the other data on Fig. 2 were deduced from either RBS or β-backscattering measurements. RBS determination of W areal coverage on Si is accurate to ±2%. Therefore, the thicknesses plotted for these data are derived from the measured areal coverage of W and the assumption of full W density. We will shortly show that the assumption of full density, and therefore the calculation of film thickness, is often erroneous.

Figures 1 and 2 present data that are interesting from both scientific and technological standpoints. First, it will be interesting to understand the temperature dependence of W growth. The widely varying data of Fig. 2, probably due to subtle differences in wafer cleaning and loading, suggest that surface condition is critical to film growth behavior. On the other hand, from a practical standpoint, thick W film growth, such as is observed in Fig. 1 at 340°C, can be disastrous for devices. 1800Å of Si were consumed in the formation of that film. Since device source/drain junctions for micron-scale design rule technologies are of this order, such initial W film growth would almost completely destroy these junctions.

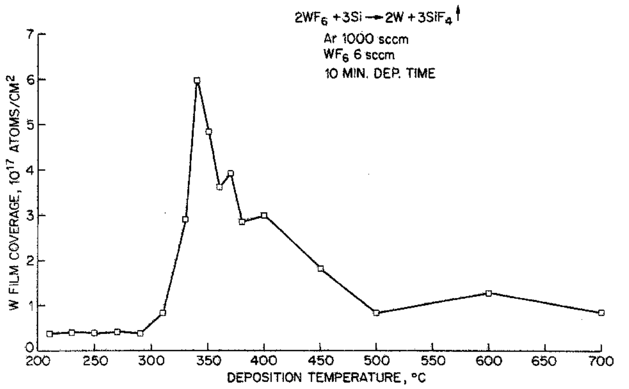


Fig. 1. W film coverage as a function of deposition temperature for lightly doped Si (100) wafers. Assuming full density of W, 10^{17} atom/cm^2 coverage equals 159.3Å of W.

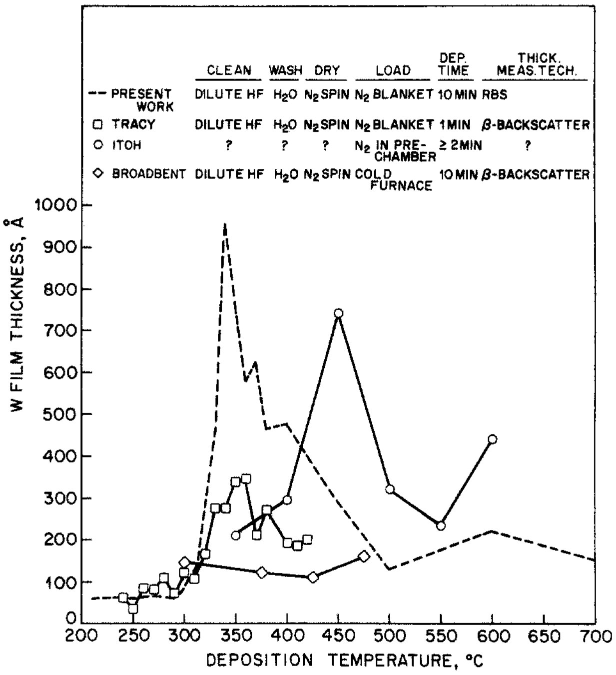


Fig. 2. W film thickness as a function of deposition temperature. Data from a variety of sources is plotted along with the data of Fig. 1.

Our previous paper (10) shows that crystal defects due to ion-implantation can greatly enhance the Si consumption reaction, *i.e.*, shift the peak of Fig. 1 to lower temperatures [see Fig. 5 of (10)]. Residual defects after implant anneal and drive-in, as well as reactive-ion etch damage, might have the same effect. Thus, differences in growth behavior at the same deposition temperature, due to different silicon processing variables, can result in en-

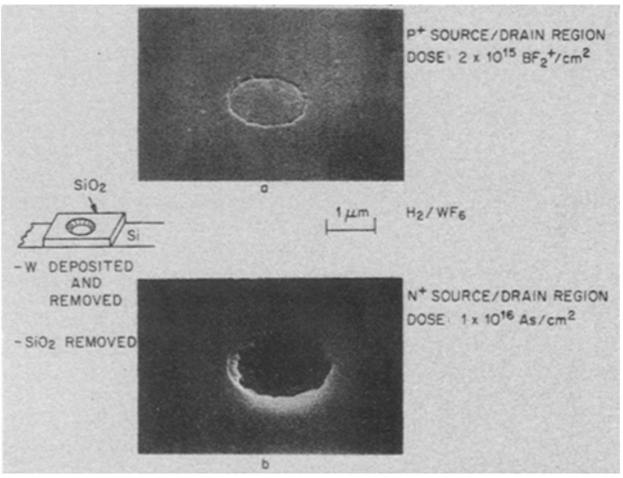


Fig. 3. Two views of Si surfaces near implanted (source or drain) regions on an actual device. Selective CVD W was deposited in windows through SiO_2 that defined these regions. (The windows were opened by dry etching.) Deposition took place at 290°C with H_2 flow = 1500 sccm, WF_6 flow 6 sccm. W and SiO_2 were then wet chemically removed, revealing the erosion of the Si due to the initial stage of the deposition, the Si reduction of WF_6 (a) P^+ region, implanted with BF_2^+, 2 × 10^{15} cm^{-2} dose, and (b) N^+ region, implanted with As, 1 × 10^{16} cm^{-2} dose. Implants were driven in and activated at 950°C for 1h before W deposition.

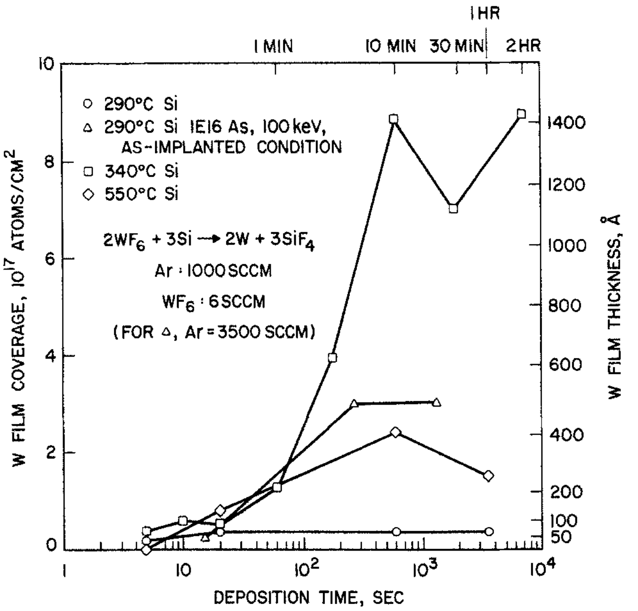


Fig. 4. W film coverage and thickness as a function of deposition time for deposition temperatures of 290°, 340°, and 550°C.

hanced erosion (*i.e.*, thick W film formation) of device features, as is illustrated in Fig. 3, also from Ref. (10). Clearly, the origins of the temperature dependence of the Si reduction reaction must be understood.

Results

Thick and thin self-limiting W films by Si reduction of WF_6.—Conventional wisdom in the CVD W field has stated many times that the Si displacement reaction, Eq. [1], results in thin (~100Å), self-limiting films of W. The data of Fig. 1 and 2 have now completely upset this simple picture. In addition, Tsao *et al.* (15) have seen Si-reduced W films as thick as ~2000Å and Mianowski *et al.* (16) have seen similar films up to 6000Å thick when deposited in a N_2 ambient at atmospheric pressure. Also, Mo films as thick as several microns have been deposited by Si reduction of MoF_6, a reaction analogous to Eq. [1] (17).

The Si reduction reaction does in fact result in self-limiting films, but not all films are self-limiting at the same thickness. Figure 4, for example, illustrates the effect of time on the growth of various Si-reduced W films. Each data point represents an individual deposition run, and the run-to-run variations can be seen. However, the self-limiting trend is clear, in that somewhere between 3 and 10 min, probably closer to 3 min, the films attain their ultimate thickness. Films deposited at 340°C self-limit at $t \sim 1300$Å, whereas those deposited at 290°C self-limit at $t < 100$Å. Figure 5, which shows the effect of WF_6 flow rate on W film formation, further illustrates the point. Once a certain flow rate of WF_6 is reached, in this case somewhere between 1 and 6 sccm, W film thickness reaches its ultimate value. Further increases in WF_6 flow, even up to 30 sccm, do not significantly affect the self-limiting behavior, whether thick films (at 340°C) or thin films (at 290°C) result.

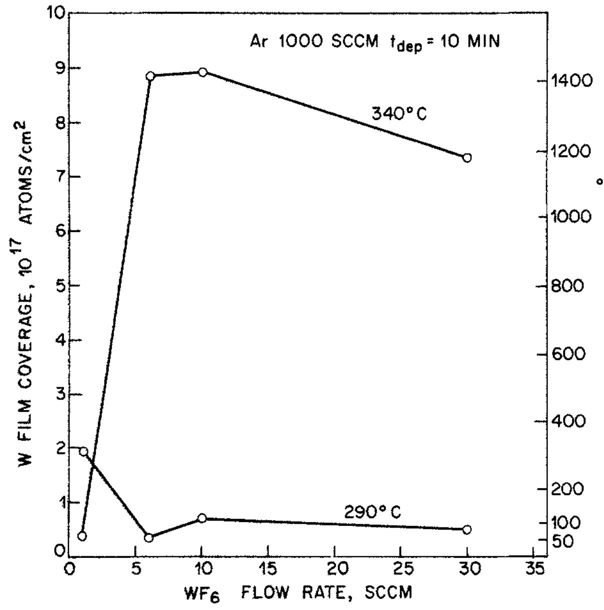
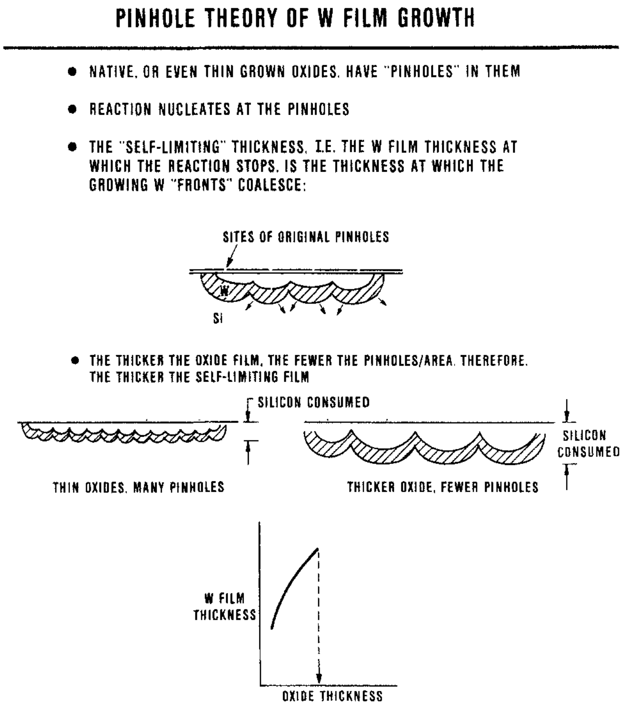


Fig. 5. W film coverage and thickness as a function of WF_6 flow rate, at 290° and 340°C.

These new findings, as well as the data in Fig. 1 and 2, and the recent observations in the literature (15-17), must change the way we think about the Si displacement reaction. First, we must ask how it is possible for thick W films to grow by what is supposed to be a diffusion controlled reaction that is traditionally thought to self-limit when the W thickness is about 100Å. Furthermore, now that it is well established that thick W films are a reality, we must ask why all W films produced by Si reduction are not thick, especially those formed at $T > 340$°C. Finally, we should ask why the thick W films do not grow thicker with increased time and WF_6 flow. Why are they self-limiting at all?

One model to explain thick W film growth by Si reduction of WF_6 is what we will call the pinhole theory of growth, illustrated in Fig. 6. Much of this model has been proposed by Broadbent *et al.* (14). It is known that Si surfaces have a thin (~5Å) native oxide on them (18), which quickly regrows after cleaning. This oxide is assumed to be imperfect and therefore has pinholes in it. The Si reduction reaction is assumed to nucleate at these pinholes, and advance into the underlying silicon. The self-limiting thickness is the thickness at which the reaction stops, which is thought to happen when the growing fronts coalesce. The W film thickness at which this happens will be related to the original pinhole density. Many pinholes should give rise to many small growth fronts, and a W film that coalesces quickly, *i.e.*, a thin film. Few pinholes, then, should lead to just a few growth fronts, which will have to consume a lot of Si before coalescing, thereby giving rise to a thick W film. Furthermore, if one assumes that pinhole density decreases as oxide thickness increases (*i.e.*, thicker oxides are more perfect), then one should see W film thickness *vs.* oxide thickness be-


PINHOLE THEORY OF W FILM GROWTH

- NATIVE, OR EVEN THIN GROWN OXIDES, HAVE "PINHOLES" IN THEM
- REACTION NUCLEATES AT THE PINHOLES
- THE "SELF-LIMITING" THICKNESS, I.E. THE W FILM THICKNESS AT WHICH THE REACTION STOPS, IS THE THICKNESS AT WHICH THE GROWING W "FRONTS" COALESCE:
- THE THICKER THE OXIDE FILM, THE FEWER THE PINHOLES/AREA. THEREFORE, THE THICKER THE SELF-LIMITING FILM

Fig. 6. The pinhole model of W film growth by Si reduction of WF_6

havior similar to that depicted at the bottom of Fig. 6. Naturally, when the oxide gets thick enough, no W is deposited by Si reduction.

In fact, recent work (19) has demonstrated this predicted behavior, with a peak W film thickness of about 1000Å for an oxide thickness of ~20Å. In spite of the agreement between the predicted and experimentally determined forms of the growth behavior, the pinhole theory of growth is rather unsatisfactory. For one thing, if growth of the W film is diffusion limited (by either Si or WF_6 diffusion through the growing W film), then the growth along each front should be self-limited and the growing fronts should not coalesce. Growth should only proceed laterally under the native oxide. In other words, perhaps just a few monolayers of continuous W should be enough to stop the Si reduction reaction. The fact that this does not happen suggests that discontinuous films of W form, and that a pinhole argument may only partially explain the data of Ref. (19). We will show shortly that Si-reduced W films are in fact very discontinuous.

Furthermore, RBS and spectroscopic ellipsometry (20, 21) were used to characterize the surface of clean Si wafers that underwent simulated W deposition runs, *i.e.*, were removed from the furnace just prior to W deposition. Figure 7, which illustrates these results, reveals that very little change in native oxide thickness is noted in the temperature range 300°-350°C, where, according to Fig. 1, very significant changes in W deposition behavior were noted. That a major change in W deposition behavior can be precipitated with only negligible change in oxide thickness suggests that the pinhole theory of growth does not have much validity. Note from Fig. 7 that a simulation temperature greater than 350°C is required before significant process-related oxide growth is seen. Even then, it is observed that this oxide growth is not associated with enhanced W film growth, as can be seen in Fig. 1. W film growth can be greatly diminished by leaving the samples in the furnace for 2h before deposition, at *e.g.*, 340°C, or by introducing the sample at 700°C and slowly cooling it under vacuum, to the deposition temperature of, *e.g.*, 290°C. In both cases, very thin (≤100Å) W films result, due to the presence of a thicker native oxide (Fig. 7) and also carbonaceous layers, which are detectable by Auger analysis or spectroscopic ellipsometry studies. In fact, about 5-10Å of carbonaceous material is found on cleaned Si surfaces, and, because of its optical similarity to SiO_2, when added to the 5Å of real native oxide, it accounts for the "15Å" of native oxide commonly reported for cleaned Si by ellipsometry measurements.

A final aspect of the pinhole theory that is troublesome is its assumption that the native SiO_2 layer remains intact, and that attack of the Si takes place through and underneath it. In fact, the native oxide is not stable in the presence of WF_6

$$3SiO_2 + 2WF_6 \rightarrow 2WO_3 + 3SiF_4 \qquad [3]$$

with $\Delta G = -48$ kcal/mol of WO_3 at 327°C. Due to the destruction of the SiO_2 film, a model as simple as the pinhole model probably only has limited validity.

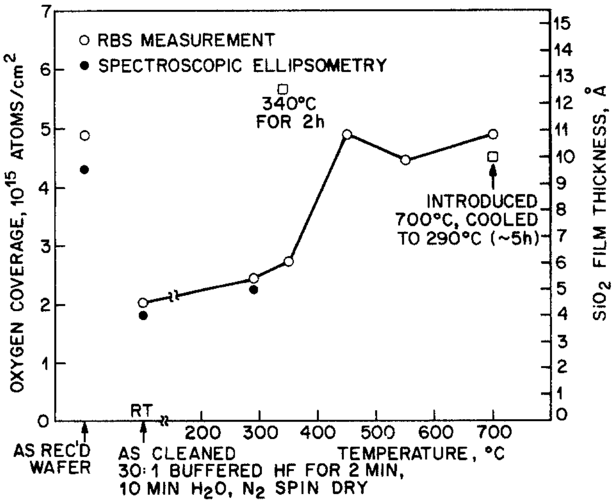


Fig. 7. Oxide coverage on Si(100) as a function of deposition (simulated) temperature. Samples held at temperature for about 15 min (except where noted), then removed prior to deposition.

The preceding discussions, and the evidence of Fig. 1, suggest that there is no kinetic limitation to the formation of CVD W by Si reduction. That a very thick film forms at 340°C but not at 310°C indicates that growth is not a diffusion limited process, since it is unlikely that the temperature dependence of the diffusion mechanism is that strong. Even assuming it was that strong, why would growth suddenly decrease after only a slight further increase in temperature to, *e.g.*, 375°C? It is more likely that the temperature dependence of CVD W film growth by Si reduction is controlled by factors such as the temperature dependence of nucleation rate, sticking coefficient, atomic reduction mechanism, and other mechanisms. To study these effects, sophisticated surface chemistry studies, performed in high vacuum with very good diagnostic techniques such as Auger spectroscopy, RHEED, XPS, and mass spectrometry need to be carried out.

Film Structure.—Table I summarizes an experimental fact that was repeatedly observed. W film thicknesses, calculated from RBS measurements using W full density, were consistently smaller than actual film thicknesses as observed by TEM cross section. The ratio of the two thickness measurements is equal to the density of the W film, as expressed as a fraction of its full density. Thus, CVD W films, deposited at a variety of temperatures, are all less than full density. It is interesting to note that the W film density peaks at about the same temperature as the growth maximum (~340°C) and that it follows the behavior of Fig. 1 in general. The percentage of space not occupied by W (*i.e.*, trapped gases, pores, inclusions) in the CVD W films varies from 40 to 58.8%. Careful scrutiny of the RBS spectra reveals less than 2% Si in the W films, the detectability limit by RBS.

The discontinuous, porous nature of the Si-reduced W films is illustrated in the next two figures. Figure 8 is a plan view TEM photomicrograph of a W film deposited on Si. The sample was prepared by thinning it from the back (Si) side using wet chemical techniques and ion milling. The hole in the sample thus created is towards the right center of the picture. Therefore, the thickness of the TEM sample decreases from left to right, and two types of porosity become obvious. The first is intergranular porosity due to sample thinning. These regions are formed between coalescing W grains, during growth, and punch through more quickly during thinning for TEM. The second form of porosity is intragranular and is observable in the grains at the right of Fig. 8. This porosity is finely distributed, on the order of ~25Å. Figure 9 illustrates the intragranular porosity in more detail. In this darkfield TEM photomicrograph, it can be seen that certain W grains are diffracting strongly. It is further seen that each grain is composed of tiny particles separated by a fine pore network. The grains are therefore "spongy," and reminiscent of a partially sintered mass of particles. From Fig. 9, the particles that form the grains can be seen to be about 25-200Å in size.

The origin of the porous structure of the W films seems quite obvious. Since a gas (SiF_4) is evolved during the formation of the W deposits, disruption of the film is to be expected. For example, if a nucleating SiF_4 "bubble"

Table I. Volume percent W in Si reduced W films

(100)Si wafers exposed to WF_6 for 10 min with 6 sccm WF_6 and 1000 sccm Ar

Deposition temperature, °C	t_{RBS}, Å	t_{TEM}, Å (avg)	t_{RBS}/t_{TEM} = % full density of film
290	59	129	45.9
350	741	1236	60.0
550	392	737	53.2
700	200	485	41.2

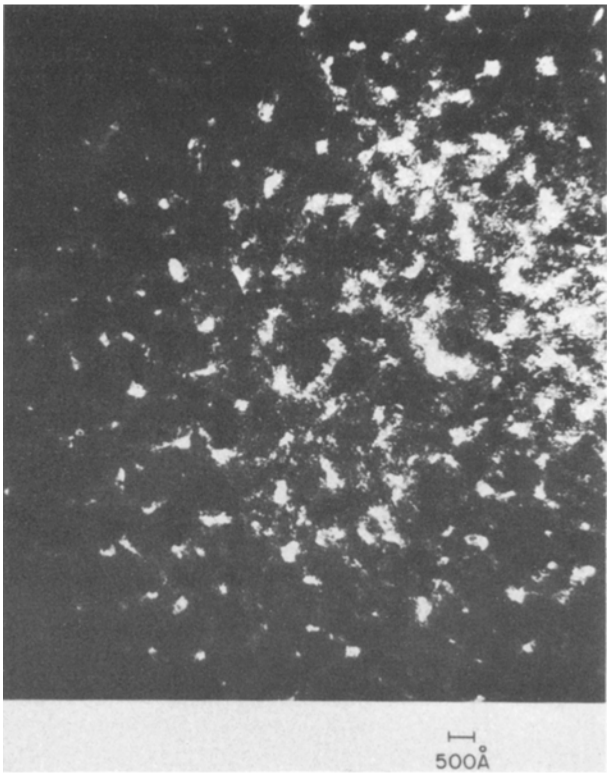


Fig. 8. Brightfield (BF) TEM photomicrograph of a Si-reduced W film, in plan view. W deposited on an amorphized Si layer, caused by implantation of As, 1×10^{16} cm^{-2} dose, at 100 keV. W film coverage is equal to 2.96×10^{17} atom/cm^2, as measured by RBS. W film was deposited at 290°C, Ar = 3500 sccm, WF_6 = 5 sccm, 4.5 min.

is occupying a site on the growing W film, somewhere near the W/Si interface, another W particle cannot nucleate there. The pores, therefore, may be the remnants of bubbles of SiF_4.

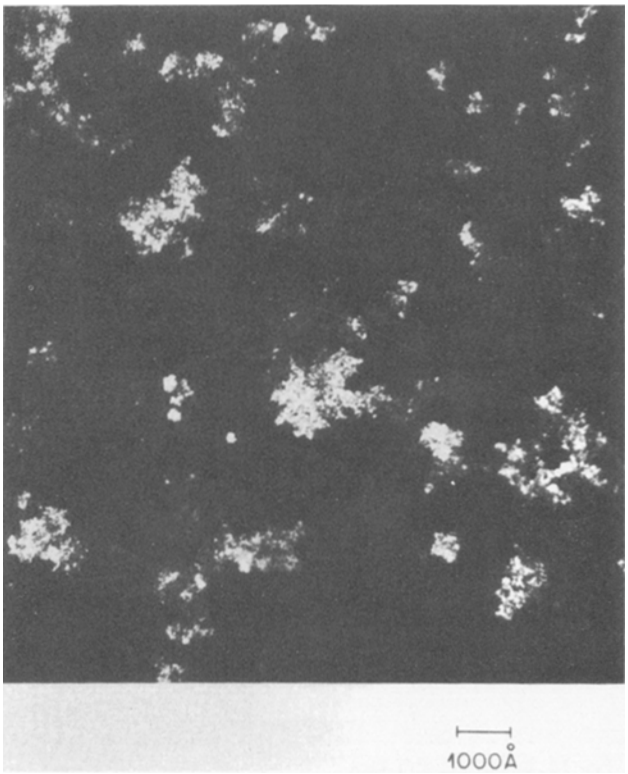


Fig. 9. Darkfield (DF) TEM photomicrograph of a Si-reduced W film, in plan view. W film was deposited at 340°C, Ar = 1000 sccm, WF_6 = 5 sccm, t = 5s.

These new observations of microporosity in Si-reduced W films are consistent with two other observations made on these films. First, since the porous W film may not be a barrier to further WF_6 in-diffusion, the porosity provides a mechanism for the growth of thick Si-reduced W films. In other words, such films are not self-limiting at small W coverages because they are not barriers to further reaction. The temperature dependence of W growth (Fig. 1) may then be dominated by W film pore structure more than anything else. Second, we have observed very high film resistivities ($50\text{-}200 \times 10^{-6}$ Ω-cm, 10-40 times the bulk W value) for Si-reduced W films. A significant portion of this increase is explained by the lack of interconnectivity of the porous W films.

Knowledge of CVD W film morphology as a function of time might offer some insight into the formation of the porosity, and also an understanding of the temperature dependence of growth. Figures 10-13 illustrate, in TEM cross section, the morphology of films deposited for 5s (a), and for 10 min (b), at temperatures of 290°, 350°, 550°, and 700°C. The TEM samples were tilted in the microscope to various degrees, to reveal more of the surface detail of the W films. Figure 10a shows that at 290°C the W film nucleates heterogeneously on the Si as small, faceted W particles. As is indicated in Table II, these particles are of the order of 124Å. It is interesting to note that the distribution of particles is a mapping of whatever nucleation sites (*i.e.*, pinholes, carbon contamination, spaces between oxide patches, etc.) existed on the Si surface. After 10 min of growth, Fig. 10b, the structural details of the film are no longer distinct. The original particles appear to have merged, and some smaller particles, that perhaps nucleated in between the original particles, can be distinguished. It is obvious from the density variations in the photomicrograph that the W film is not fully dense.

Figure 11, films deposited at 350°C, illustrates a film morphology that is very different from that observed at 290°C. This could have been anticipated by the temperature data, Fig. 1, which shows that at 350°C the W coverage is about ten times greater than at 290°C. Even after only 5s deposition time, a significant W film has formed. This film exists as blotchy patches covering the Si surface, about 204Å average size. The patches are composed

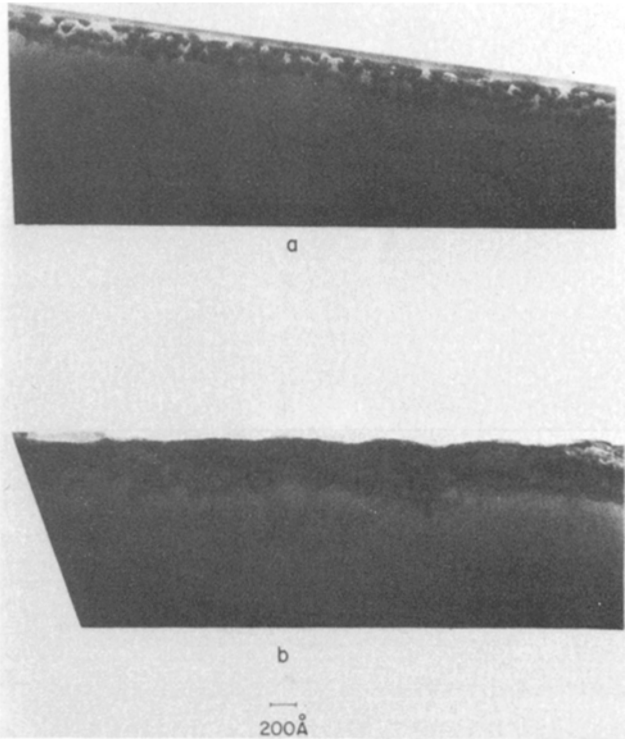


Fig. 10. Brightfield (BF) TEM cross-sectional photomicrographs of a Si-reduced W film, deposited at 290°C on a (100) Si wafer. Ar = 1000 sccm, WF_6 = 5 sccm, (a) t_{dep} = 5s and (b) t_{dep} = 10 min.

Table II. Average sizes of features observed in TEM cross sections of CVD W films

T, °C	$t_{dep} = 5s$	$t_{dep} = 10$ min
290	124Å nuclei (faceted)	Internal features of film are not distinct
350	Blotches, 204Å	Blotches, 457Å, composed of 37Å particles
550	57Å nuclei	158Å particles
700	98Å nuclei (very few)	218Å particles (grain formation)

of smaller W particles, and both the inter and intrapatch porosity are evident. The film, after 10 min of growth, looks remarkably similar to the initial stages of growth. The film is porous, the blotchy patches have enlarged to 457Å average size, and the particles comprising the patches are now discernable and are 37Å average size (Table II).

After deposition at 550°C, Fig. 12, the films begin to exhibit very distinct features. Five seconds exposure, Fig. 12a, results in a distribution of W nuclei on Si, 57Å average size, evenly dispersed on the Si surface. In contrast to the nuclei observed at 290°C, these are not faceted and appear to be very thin and planar. It is possible that these are at an earlier stage of growth than those at 290°C. The film that results after 10 min exposure, Fig. 12b, seems to have evolved by growth of the original particles, as well as secondary nucleation and growth to consume the Si between the original particles. What results is a highly discontinuous (porous) film composed of particles of 155Å average size.

Nucleating particles were hard to observe on the 700°C sample, Fig. 13a. The few that were observed were similar to those seen at 550°C. After 10 min at 700°C, Fig. 13b, the film that is deposited is similar to that of 550°C, except that some sintering of the film can be observed through the formation of distinct W grains, 210Å average size. No silicide formation was observed by electron diffraction analysis.

We have also observed that under certain conditions, the W films nucleate as β-W, the A15 cubic form, rather than α-W, the more common bcc form. Figure 14 illustrates the electron diffraction patterns of β-W (a), and α-W, (b). The β-W films were observed to form on amorphized Si (as-implanted) substrates, and only then when the W film coverage was less than about 5 × 10^{16} atom/cm^2. Thicker W films were always observed to consist of the α-W phase. Furthermore, *in situ* TEM heating experiments showed that the β-W phase was stable up to a temperature of 425°C. β-W has been observed to form as a result of a variety of nonequilibrium and energetic film deposition processes (22, 23). It is also known to be stabilized by F and other impurities. Therefore, its presence in thin CVD W films is consistent with previous observations.

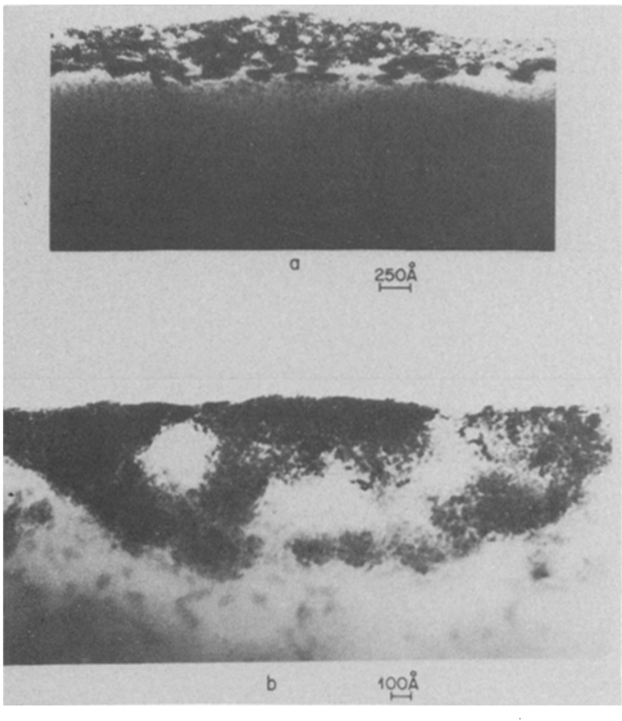


Fig. 11. Brightfield (BF) TEM cross-sectional photomicrographs of a Si-reduced W film, deposited at 350°C, on a (100) Si wafer. Ar = 1000 sccm, WF$_6$ = 5 sccm, (a) t_{dep} = 5s and (b) t_{dep} = 10 min.

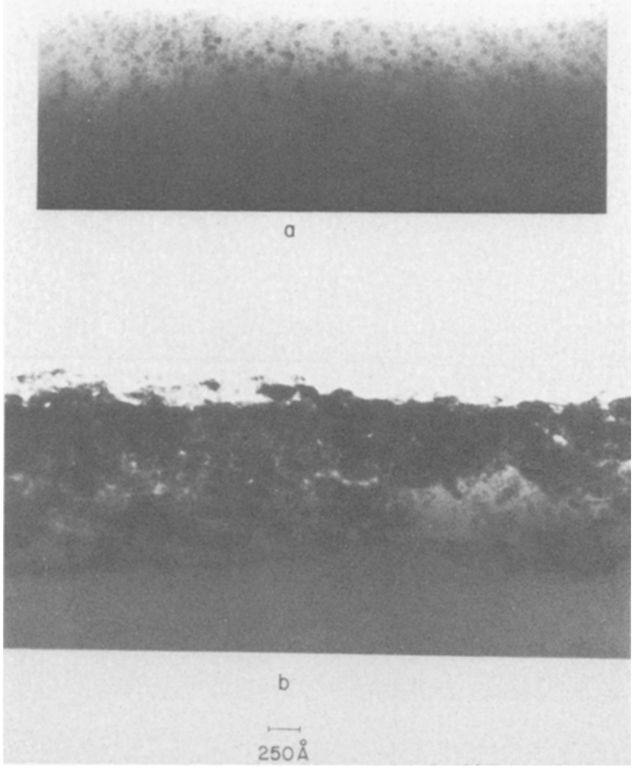


Fig. 12. Brightfield (BF) TEM cross-sectional photomicrographs of a Si-reduced W film, deposited at 550°C, on a (100) Si wafer. Ar = 1000 sccm, WF$_6$ = 5 sccm, (a) t_{dep} = 5s and (b) t_{dep} = 10 min.

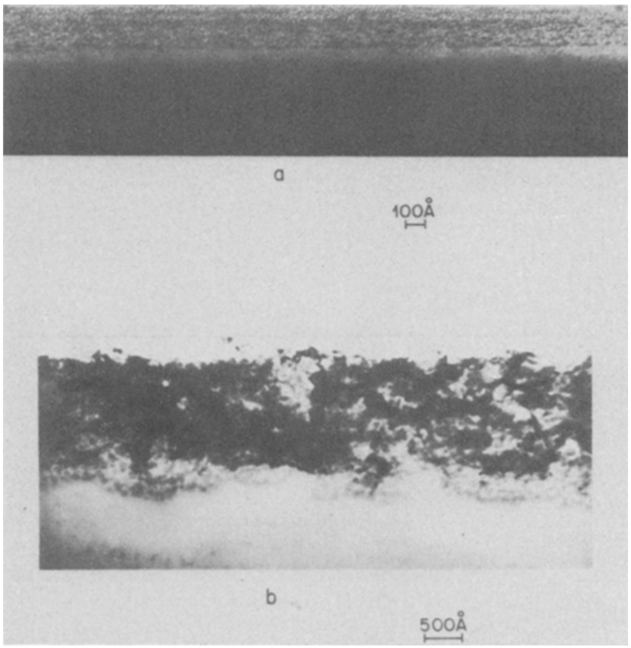


Fig. 13. Brightfield (BF) TEM cross-sectional photomicrographs of a Si-reduced W film, deposited at 700°C, on a (100) Si wafer. Ar = 1000 sccm, WF$_6$ = 5 sccm, (a) t_{dep} = 5s and (b) t_{dep} = 10 min. The fuzzy band at the top of Fig. 13a is the mounting epoxy for the TEM sample.

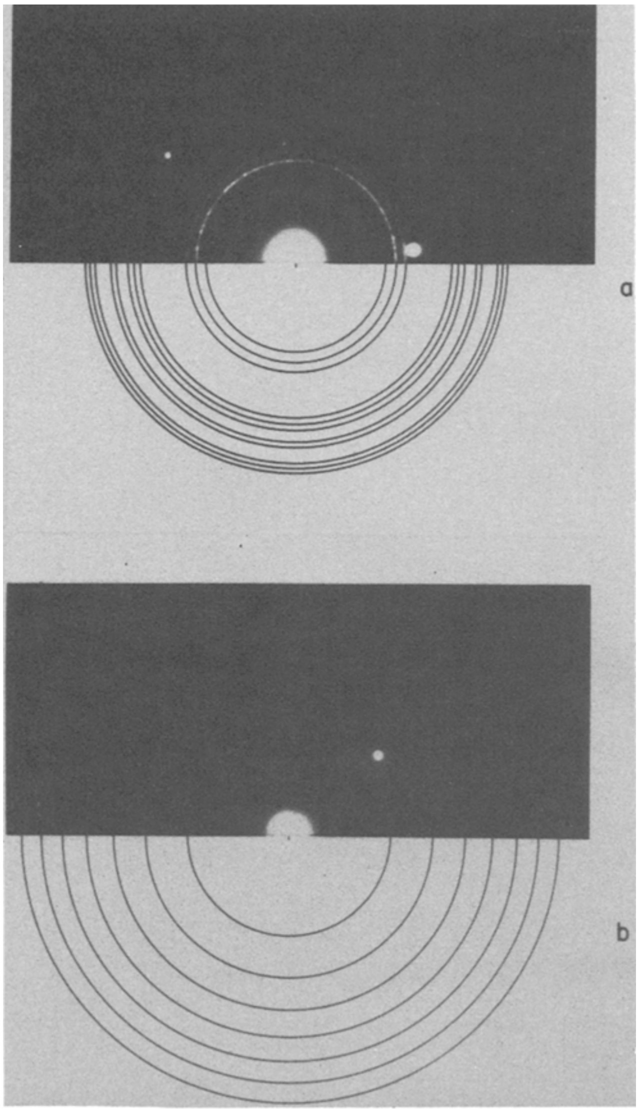


Fig. 14. Selected area diffraction patterns and computer simulations for (a) β-W, and (b) α-W.

Discussion

The observation that Si-reduced W films are porous and discontinuous provides an obvious model for thick W film growth. The W film, previously thought to be a barrier to further contact between Si and WF_6, may not be a barrier at all. Furthermore, in spite of the morphological differences in film structure between the films grown at various temperatures, Fig. 10b-13b, they are, according to Table I, about equally porous and probably permeable to WF_6 to about the same extent. Upon first considering the data of Fig. 1, the question one asks is how, under certain conditions, can such thick W films grow? However, given the discontinuous, porous nature of these films, one should ask why all Si-reduced W films are not thick, like the Mo films produced by Si reduction of MoF_6. These films (17) have been found to be porous to about the same extent as the present W films, and are capable of forming to a thickness of several microns. We believe that both W and Mo films form by the same mechanism, that of fluoride percolation through the porous metal film. Why the Mo films tend to grow an order of magnitude greater than the W films is not understood.

We believe that the answer to this question will not be resolved until the detailed mechanism of the WF_6-Si reaction is understood. The temperature dependence of W film growth, as observed in Fig. 1, is probably due to the temperature dependence of the sticking coefficient, desorption coefficient, etc., of one of the reaction intermediates. The appeal of such a catalytic model is that it has the potential to explain the effects of minor surface modifications on W growth behavior, Fig. 2, and also to explain the data of Fig. 1 in terms of "poisoning" phenomena. Self-limiting behavior, independent of the W film thickness at which it occurs, is consistent with such a mechanism.

Studies are now underway (24) to understand the reaction of WF_6 with Si clusters of various sizes. Such studies may eventually lead to the determination of the rate limiting step of the reaction between WF_6 and bulk Si. High vacuum, *in situ* reaction studies on carefully cleaned and characterized Si surfaces are also needed to solve this problem. High vacuum diagnostics such as RHEED, Auger spectroscopy, mass spectrometry, and x-ray photoelectron spectroscopy are needed to understand the initial stages of the WF_6-Si reaction.

That the W films are probably permeable to WF_6 discredits the already weakened pinhole theory of growth. Of course, as is observed in, *e.g.*, Fig. 10a, growth starts at some sort of nuclei. The nature of the nucleation site is not known now, but it is unlikely to be a pinhole in the native oxide, since the native oxide is only about 5Å thick and most probably exists as patches of oxide on the Si surface. The nucleation sites may be Si areas in between the oxide patches, or discontinuities in the carbonaceous layer that is known to exist on the Si surface along with the oxide.

As interesting as the origin of thick W film growth is from a scientific standpoint, it must be avoided from a practical standpoint. Although the growth of W films by Si reduction of WF_6, in the presence of H_2, has not been extensively studied, it is at least known, from *e.g.*, Fig. 3, that under certain circumstances, thick W growth is possible. Several solutions now exist to ensure that excessive consumption of Si does not occur. First, film growth can be limited to the temperature regime below 300° and above 500°C, thus avoiding the enhanced growth temperature regime. One drawback to this solution is the fact that selective growth may be hampered at temperatures of 500°C and above. A second solution would involve the use of excess SiF_4 (8) to suppress the Si reduction of WF_6. This has been shown to minimize Si consumption, and, as a bonus, decrease contact resistance to Si, but other effects, such as leakage current in devices prepared in that way, have to be studied further. A final solution, suggested by (13), involves the introduction of the wafers into a cold furnace. This solution is not practical for the hot wall, multiple wafer reactors used today, but is certainly applicable for the cold wall, single wafer CVD reactors that may dominate in the future.

Finally, we would like to comment on the lack of "wormhole," or "tunnel" defects (3, 4, 25) in the Si-reduced W films. Due to their similarity with defects generated during the catalytic hydrogenation (26) or oxidation (27) of graphite, we have ascribed (4) the production of these defects to the catalytic gasification of Si by HF

$$Si + 4HF \rightarrow SiF_4 + 2H_2 \qquad [4]$$

for which $\Delta G = -90$ kcal/mol of Si at 300°C. Since HF is necessary for this reaction to occur, and since HF is a byproduct of the H_2 reduction of WF_6, one should not expect to see wormhole defects in Si-reduced W films. Stacy *et al.* (25) claim to see them in such films, but the feature they observe may be nothing more than a W particle formed by Si reduction and embedded in the Si matrix.

Summary

We have studied the formation and structure of CVD W films deposited by the Si reduction of WF_6, in the temperature range 210°-700°C. Rutherford backscattering spectroscopy and transmission electron microscopy were the primary diagnostic techniques used. Although the great majority of CVD W films deposited for IC applications are deposited by H_2 reduction, the Si reduction of WF_6 always occurs first, even in the presence of copious amounts of H_2. Therefore, it is the Si reduction reaction that determines the nature of the W/Si interface, and, in turn, such important properties as contact resistance and leakage current.

We had previously reported that in this temperature range, the growth of the films exhibited an unusual temperature dependence. Between 210° and 310°C, the films self-limit at about 0.3×10^{17} atom/cm^2 (~60Å, assuming full dense W) coverage of W. In the temperature range 320°-450°C, coverages up to 6.1×10^{17} atom/cm^2 (~950Å at 340°C), are observed. In the higher temperature range, 500°-700°C, film coverages of about 1.5×10^{17} atom/cm^2 (200Å) are observed. All films, thick or thin, are found to be self-limiting. That is, once a certain deposition time (about 3 min) is past, or a certain WF_6 flow rate (about 6 sccm) is established, the films achieve their ultimate thickness; further increases in deposition time or WF_6 flow rate cause negligible changes in film thickness.

TEM and RBS results show that the films are discontinuous and porous, regardless of the deposition temperature. The discontinuous nature of the films provides a simple mechanism for the growth of thick W films by Si reduction, *i.e.*, the percolation of WF_6 to the Si. Such thick films have been observed with increasing frequency as of late and have been enigmatic, because it has long been assumed that a thin W film (~100Å) could prevent Si and WF_6 from reacting, thus self-limiting the film. The lack of interconnectivity of these films also explains their high resistivity.

It is suggested that since thick W films by Si reduction of WF_6 are a reality, and that the discontinuous nature of the W films is a likely mechanism for the growth of such films, that the temperature dependence of W film growth is controlled by some surface catalyzed reaction. Thus, the temperature dependence of the sticking coefficient of some reactive intermediate probably controls the reactions. Such a model has the potential to explain the self-limiting behavior of the reaction, *e.g.*, by catalytic poisoning at some stage of film growth, and the dramatic effects of minor changes of the Si surface (*i.e.*, due to cleaning variations) on W film growth behavior. We believe that high-vacuum, *in situ* reaction studies have to be carried out using a variety of diagnostic techniques before an understanding of the reaction mechanism will be reached.

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