論 文
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LPCVD를 사용하여 WF_6의 교번적 수소환원 반응에 의한 새로운 선택적 텅스텐 박막 증착

New Selective Tungsten Deposition Process by the Alternating Cyclic Hydrogen Reduction of WF_6 using LPCVD

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요 약

본 논문은 LPCVD를 사용하여 수소환원반응의 교번(alternating cycle : a.c.) 방법으로 Si위에만 선택적으로 텅스텐 박막을 증착하는 공정개발의 연구결과를 설명한다. 이러한 a.c. 방법은 WF_6의 수소환원반응에 바로 뒤이어 W와 WF_6 가스의 disproportionation 반응을사용하여 산화막 위의 nuclei를 제거하는 방법이며, 종전에는 보고된 바가 없는 새로운 방법이다.

이 방법에서 텅스텐 박막의 선택도는 다른 증착 파라메타를 일정하게 하였을 때, a.c. 공정에서 수소환원공정 수행시간과 불수행 즉 disproportionation 반응시간의 비율 및 총 증착 시간에 영향을 받는다.

본 연구에서 여러가지 모형의 Si와 SiO_2로 구성된 웨이퍼 위에 Si 위에만 텅스텐 박막두께 420nm까지 선택성이 좋은 텅스텐 박막을 증착할 수 있었으며, 이때의 조건은 수소환원시간/disproportionation 시간이 30초/15초의 교번시간, 기압1 Torr, 온도 400℃ 및 H_2, Ar, WF_6 가스유량이 각각 500sccm, 400sccm, 50sccm 이었다.

또한 a.c. 공정 30초/10초 로는 온도 450℃, 400℃ 및 350℃에서도 좋은 결과를 얻을 수 있었다.

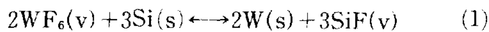
Abstract- New selective tungsten deposition on silicon process is described which makes use of a previously unreported, alternating cyclic, "A.C.", deposition of tungsten. In this a.c. process, the hydrogen reduction of hexafluoride is followed cyclicly by the removal of incipient (precursor) nuclei which may have begun to grow on the oxide mask via the use of the disproportionation reaction involving tungsten and its hexafluoride. The selectivity of the tungsten films is affected primarily, other deposition parameters being held constant, by the ratio of the on-to -off cycles in the a.c. sequence, as well as by the absolute times for each portion of the total cycle. In the studies described, excellent selectivity was obtained for tungsten thicknesses up to 420nm, on a variety of oxide masked silicon wafers.
These results were achieved with a hydrogen flow rate of 500 sccm, and argon flow rate of 400 sccm, and a tungsten hexafluoride flow rate of 50 sccm, at 1 Torr and 400°C in a 30 seconds / 15 seconds (30"/15"), reduction/disproportionation a.c. sequence. Good results were also obtained with a 30"/ 10" ratio at 450°C, 400°C and 350°C. Using hydrogen reduction alone, under otherwise identical conditions, selectivity was always lost at about 200 - 250 nm.

1. INTRODUCTION

Tungsten is an attractive metal for a number of applications in silicon based VLSI/ULSI for several reasons.[1]

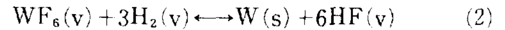
While most of the extensive literature of the past decade has dealt with the blanket deposition of tungsten, there has also been considerable interest,[2, 3]though less success in depositing tungsten selectively into exposed silicon regions in SiO_2 masked surfaces. A selective tungsten deposition process, STD, offers the promise of dispensing with related lithographic/etching sequences, enabling utilization of tighter device/circuit design groundrules. Such a self aligned technique would of course be simpler than its lithographic counterpart, and therefore economically advantageous. While a lift-off patterning might accomplish the same thing in certain applications, it would not be as simple to implement.

Attempts at selective processes, have been based on the use of two concomitant reaction sequences [4, 5] (conducted in a Low Pressure Chemical Vapor Deposition, LPCVD, environment, generally in a hot wall reactor). STD is initiated (even in the presence of H_2) by reduction of the hexafluoride of tungsten by exposed silicon to form the metal and volatile SiF_4, as depicted in equation 1.



$$2WF_6(v)+3Si(s)\longleftrightarrow 2W(s)+3SiF(v) \qquad (1)$$

This selective "displacement-reduction" reaction appears to be self-limiting at tungsten film thicknesse ranging from 15-40nm. Self-limiting growth appears to occur when the hexafluoride of tungsten is unable to diffuse through the already deposited tungsten fast enough to continue reacting with the underlying silicon. Continued deposition of the tungsten is then obtained due to the presence of the hydrogen which reduces the hexahalide, as depicted in Equation 2.



$$WF_6(v)+3H_2(v)\longleftrightarrow W(s)+6HF(v) \qquad (2)$$

In order to retain selectivity employing Equation 2, two onditions must obtain. The first is that the SiO_2 must be inefficient in initiating the reduction process heterogeneously on its surface, and probably more important, if it does initiate the process, the sticking coefficient of tungsten to SiO_2, under the conditions of the experiment, must be significantly lower than to already deposited tungsten. At temperatures $\leq 400°$ C, a reasonable degree of selectivity is obtained to a maximum thickness of about 200~250nm, after which spurious nucleation occurs on the oxide mask.

Attempts to extend this limit by incorporating SiH_4 in the reacting gas, for example,[6, 7] have not provided consistent improvement, but do enhance the growth rate in blanket deposition processes[8]. This limiting thickness makes it difficult to employ STD to its fullest potential in via-fill applications. Once spurious nuclei have formed, they grow rapidly, and selectivity is totally lost.

To understand and solve this problem, the mechanism of selectivity loss has been studied, with the focus being on the reaction by-products, particularly on the desorption of WF_x[9], the adsorption of similar species[10], the adsorption of tungsten itself[11], as well as the adsorption of $Sif_x(x=2, 3)$[12]. Despite such efforts, the fundemental mechanism(s) responsible for the loss of selectivity has not been identified, nor has the problem been solved. It is not uncommon to hear talk of needing an oxide surface which has been "poisoned". By this is meant that spurious nucleation is retarded. Such a description conjures up what is believed to be an incorrect assessment of why selectivity is retained or lost.

Based on an assumption that selectivity, or lack thereof is dependent strongly on the relative mean free paths of depositing tungsten on 1-oxide masks, and 2-on already depositied tungsten, as well as 3-the relative expanses of oxide and tungsten filled openings, it was concluded that incipient, or precursor nucleation (we define an incipient, or precursor nucleus as one which may or may

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not grow depending upon its surface area compared to that of adjacent incipient or precursor nuclei) would always be occurring. Consequently, it would not be a question of whether or not nuclei are forming, but rather how easy it is to form them, how many are forming, what their sizes are, how many of them continue to grow, and what rate they grow. This number and size distribution would, in turn be dependent specifically on the details of the specific mask topology, i.e. the fraction of the surface covered by SiO_2, and specific mask and mask opening dimensions, as well as other factors, e.g. surface condition, and reactor parameters such as temperature, pressures, gas phase composition, linear gas stream velocity, etc. When and how selectivity is lost depends, therefore, on the stability of the formed nuclei, and how rapidly some can grow at the expense of others. If we accept the premise, therefore, that such incipient nuclei are always forming, then the path to STD becomes somewhat more obvious. Rather than trying to prevent the formation of incipient nuclei, it would be much easier to employ chemical means to cause their annihilation.

The approach to the present work predicated on these speculations, and led to the following effective solution. Since the incipient nuclei possess a greater surface energy than depostited tungsten films, one can visualize that the means for maintaining selectivity to any desired thickness would be to employ a continuously interrupted deposition process which we term an Alternating Cyclic, A.C., deposition process. During the cyclicly interrupted deposition, the incipient nuclei could be brought into the vapor phase via a disproportionation reaction[18], for example. At some other system location, perhaps the reactor walls, the etching reaction could be reversed, and vaporized tungsten could be made to redeposit.

2. DISPROPORTIONATION REACTION

Since the disproportionation reaction involving tungsten hexafluoride and tungsten, Eq. 3, for the reaction as written, has a negative enthalpy of reaction, the removal of incipient nuclei (and to some degree tungsten deposited in vias) would occur in a cold to hot process. If desired, a hot tungsten "getter" filament downstream of the wafers could be used as a collector. Thus, if during the hydrogen reduction of tungsten hexafluoride, the a.c., etching was initiated by turning off the hydrogen flow periodically, the precursor nuclei, primarily because of their high surface energy would etch rapidly, and be brought into the vapor phase. If the frequency of the a.c. process was optimized, the loss of tungsten from regions where its deposition was desired would be small. In the case of the disproportaionation reaction depicted by Eq. 3 as indicated.

$$W(s) + 5WF_6(v) \rightleftarrows 6WF_5(v) \qquad (3)$$

nature would assist the process in a hot wall system, since the natural tendency would be to move tungsten from the colder center portions of a tube reactor(the unstable incipient unclei on the oxide surface as well as the more stable filled vias) to the hotter reactor walls in a hot wall system. In general, however, for other CVD processes, it is not critical whether the reaction is hot, the cold, or cold to hot as long as at the wafer site the etching reaction occurs under the gas phase concentration-

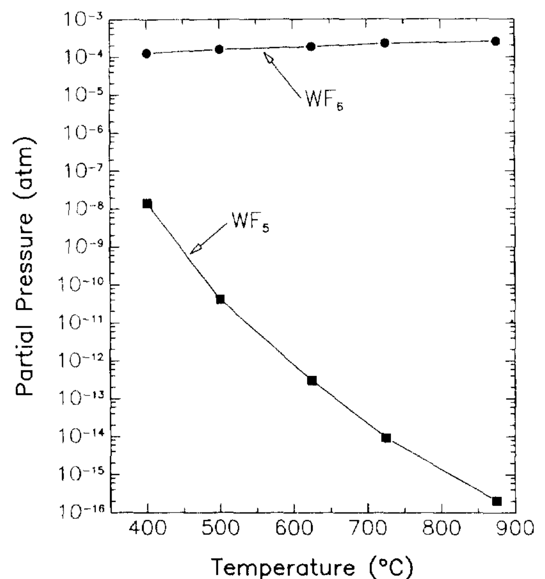


Fig. 1 Partial Pressures of WF_6 and WF_5 in the system W-F-Ar at a system pressure of 1.32×10^{-3} atm(1 torr)

temperature conditions employed.

The data for Figure 1 were calculated using the SOLGASMIX computer program [13]to determine the partial pressures of pertinent species in the ternary system W-F-Ar. From Fig. 1 these species are seen to be WF_6 and WF_5[14, 15]. It is seen further from Fig. 1 that with increasing temperatuer, the gas phase composition of WF_5 decreases. This means that in Eq. 3 the reaction has a postitive enthalpy of reaction reading from right to left. Thus, as the temperature is increased, the reaction is driven to the left. This is another way of saying that tungsten would be deposited in a cold to hot process.

3. EXPERIMENTAL PROCEDURE

Depositions were conducted on phosphorous doped 2~10Ωcm (100)-oriented 100mm patterned oxided silicon wafers. For selectivity studies, a number of differenct oxide mask patterned wafers were employed. The oxides were grown in a so-called dry-wet-dry process, dwd. On top of some of these dwd oxides, CVD oxides were deposited to a thickness of several hundred nanometers. Such composite structures simulated multi-level metal conditions where the interlevel dielectric is liable to be CVD silicon dioxide. The oxides (either that dwd oxides, or the composite dwd-CVD composites) were patterned, and then given a dilute (10 : 1 H_2O : HF)buffered oxide etch treatment for 20 sec. immediately prior to tungsten deposition.

The behavior of the selective thungsten deposition, STD, a.c. process appeared to be identical, independent of whether dwd, or composite oxide masks wer employed. The thickness of the patterned oxides also seemed unimportant (in all cases, the deposited tungsten was thinner than the masks employed). CVD oxide was grown in a 10/1 oxygen to silane mixture at 400℃. For the dwd process, the wafers were inserted into a furnace at 650℃, ramped up to 950℃ in 1% oxygen in argon, heated in oxygen for 5 minutes(') followed by a 30seconds(") purge in Ar at 950℃. Then using pyrogenic steam containing 2% HCl, the oxidation was continued at the same temperatuer for the

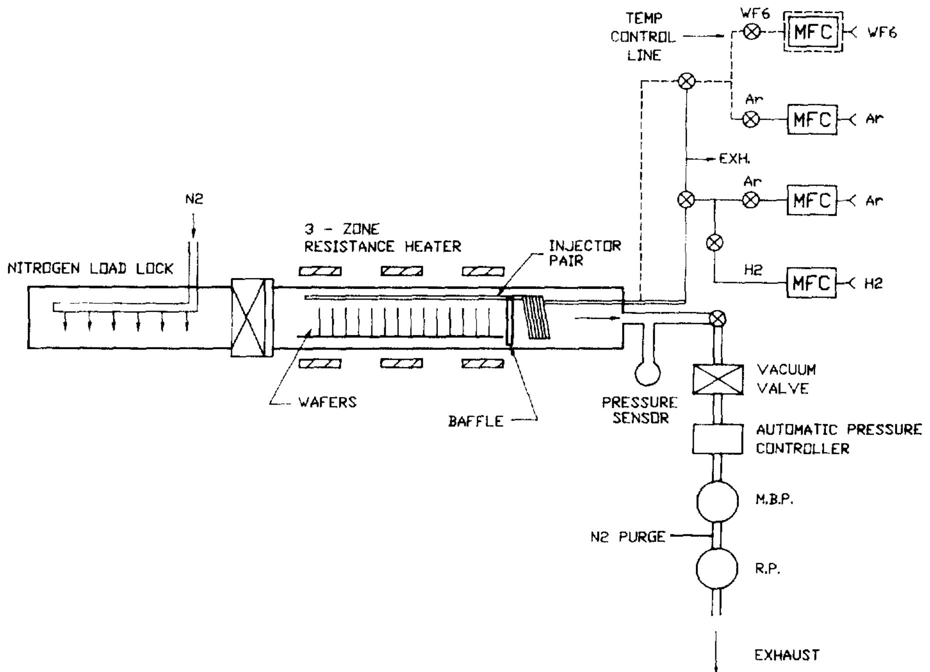


Fig. 2 Schematic diagram of tungsten LPCVD system.

time required to grow films of desired thicknesses. The dry oxidation was then resumed for another 5′. Following this final dry oxidation, the oxide was annealed in Ar for 5′, again at 950℃, and the temperature was ramped down to 650℃, before the wafers were removed from the furnace.

On one of these types of oxide masked wafers, helf of the wafer was covered with oxide, while half was etched bare. This was considered to be the most difficult test of selectivity, since incipient nuclei could develop as much as 50mm away from a bare surface. A second type of wafer contained 24 exposed 1.0㎝ on an edge squares on 1.5㎝ Other types centers in a top to bottom sequence, 2, 5, 5, 5, 5, 2. of patterned wafers contained ovals, line meanders, dumbells and circles. These were of different sizes, and different center to center spacings. Finally, wafers were also used which were completely coated with dwd oxides grown, as described above to a thickness of 350mm. These also behaved as the patterned wafers. In other words, when selectivity was good on the latter, it was good also on the completely oxide coated wafers, and when selectivity was lost on the patterned wafers, it was also lost on the completely overcoated wafers.

The apparatus in which the STD a.c. studies were conducted is shown in Fig. 2. It is identical to that used previously for blanket tungsten deposition usng the reactions depicted in Eqs. 1 and 2, [16]. Basically, via the use of an array of orifices in the injector, the reactive gas flow is from the top to the bottom of the reactor. For the present studies, unless otheriwise noted, a.c. depositions were performed at 400℃, always at a pressure of 1 Toor. The tungsten hexafluoride flow rate was always kept at 50 sccm. The H_2 flow rate during the reduction part of the a.c. depostition was always at 500 sccm, and the argon flow was maintained always at 400sccm. The wafers were first held in a load lock under a nitrogen flow of 6 1/min. The wafers were then loaded into the system which was idled at a tmeperatuer of 350℃ using a cantelever. The system itself was maintained under an argon flow. The wafers were allowed to equilibrate thermally for one hour, after which hydrogen was turned on for three minutes prior to introduction of the hexaflouride. At the conclusion of an experiment the reactor temperature was reduced to 350℃ and the cantelever was withdrawn at a rate of 12㎝/min

Each of the wafer boats contained 25 wafers. In the upstream boat, dummy wafers only were employed, while in the downstream boat, experimental wafers were alternated with dummy wafers. In both boats the wafers were spaced 4.8㎜ apart, and a fused quartz liner tube was employed in all experiments.

While a number of a.c. sequences were examined in this preliminary study, (T=350℃－450℃), the ones given the most attention, based on preliminary studies designed to define the best operational window, were 30″/10″, and 30″/15″ sequences, where the numerator in the ratio is the reduction cycle, and the denominator is the disproportionation cycle. A 30″/20″ was examined cursorily, and discontinued, because its growth rate compared to H_2 reduction alone was lower than the other two cycle ratios. Consequently, while the selectivity trend was the same as with the other cycles, this ratio was discontinued in favor of the higher net growth cycles.

The on/off cycles were controlled manually. It is to be realized that in the short cycles employed, gas phase steady state compositions could not possibly have been achieved. In addition, after being turned off, it took approximately 2 seconds for the hydrogen flow to reequilibrate through the mass flow controllers after being turned on again. Relatively however, even though steady state was not likely to be achieved, it was obvious that the cycles were experimentally significant. For example, where the 30″/15″ cycles were always selective up to at least 400nm, the selectivity of the 30″/10″ cycles, on occasionally would begin to exhibit a slight degree of non-selectivity at this thickness.

As a control for all of the a.c. experiments, straight hydrogen reduction was run on blank silicon wafers to establish maximum blanket deposition rates, as well as on patterned wafers to determine when selectivity broke down in the non a.c. process. Finally, to determine whether the observed selectivity using the a.c. technique was in part due to etching of SiO_2 by WF_6, studies

were conducted at 400℃ in which all conditions were the same as described above, except that no hydrogen was inctroduced during the process, i.e. the wafers were subjected to an uninterrupted flow of WF_6 in argon for the duration of the experiment. Such studies were conducted on completely oxided wafers for periods up to 30 minutes.

The loss of SiO_2 was less than 0.1nm/min. This indicated that SiO_2 chemical ablation was not involved in the STD process to any significant degree.

4. RESULTS AND DISCUSSION

4.1 PICTORIAL REPRESENTATIONS OF DATA

Fig. 3a and 3b show the growth of tungsten using the "standard conditions" described, in oval openings to a thickness of approximately 330nm using H_2 reduction alone, or in an a.c. mode (30″/15″ cyclerespectively. It is shown that where spurious unclei are present in 3a, they are absent in Fig, 3b. Figures, 4a and 4b show the same type of comparison in a meander pattern. The meander pattern was chosen so as to favor STD deposition in the H_2 reduction alone (Fig. 4a) by minimizing the distance between exposed silicon openings. Nontheless, it is seen that selectivity is lost in the H_2 only process, and retained in the a.c. process.

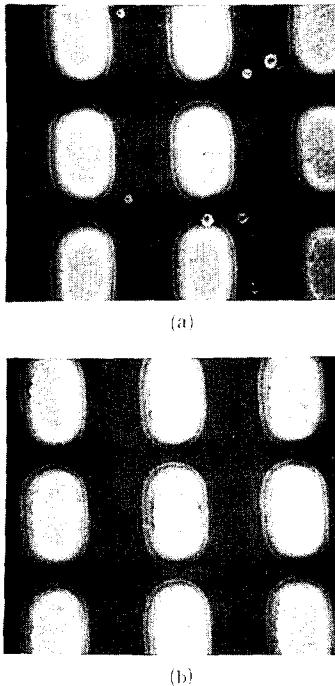


Fig. 3 SEM micrographs of tungsten on oxide patterned wafers:
(a) H_2 reduction, 330nm, and
(b) a.c. 30″/15″ cycle, 330nm.

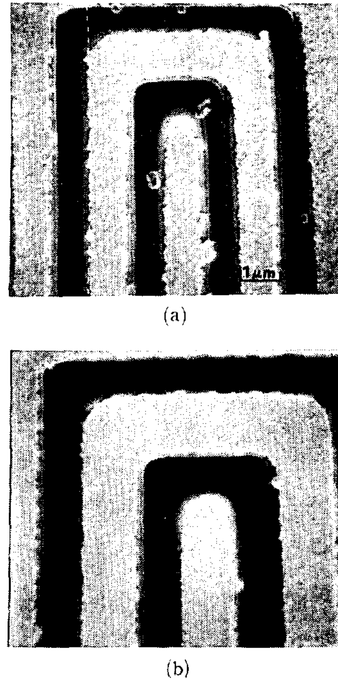


Fig. 4 SEM micrographs of tungsten on oxide patterned wafers:
(a) H_2 reduction, 330nm, and
(b) a.c. 30″/15″ cycle, 330nm.

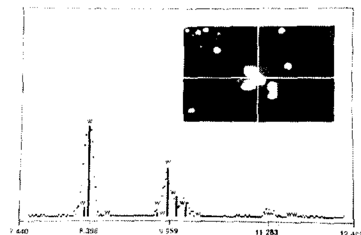
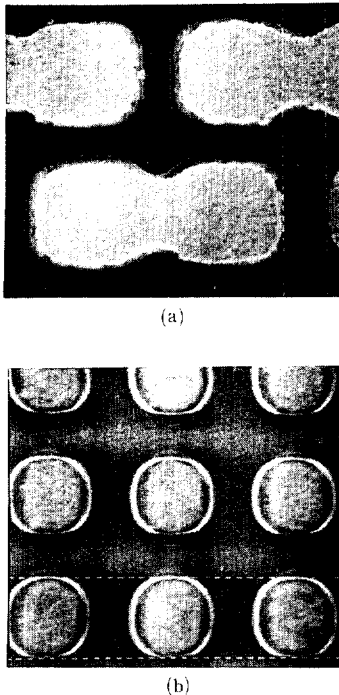


Fig. 5 X-ray dispersive analysis spectra of nuclei on SiO_2 deposited by the H_2 reduction process.



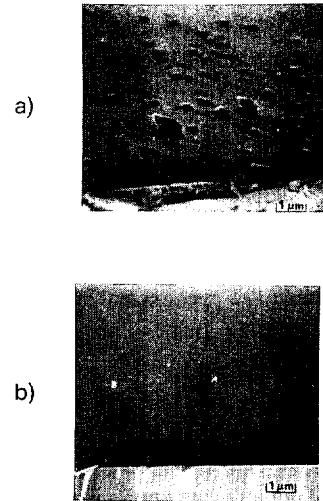
(a)

(b)

Fig. 6 SEM micrographs of 330nm a.c. Tungsten deposits at
(a) 400℃ and
(b) 350℃ : 1 torr, WF_6=50sccm H_2=500sccm, Ar=400sccm in a 30″/10″ a.c. cycle.

X-ray dispersive analysis of the particulates in Fig. 3a, and 4a is shown in Fig. 5 demonstrating that the nuclei are indeed tungsten. Fig. 6 a and 6b show a comparison of the typical results obtained with a dumbell structure, and a circular pattern at 400℃ and 350℃ respectively in a 30″/10″a.c. process for the same thickness of tungsten as in the previous picutres. It is seen that selectivity is quite good for both patterns.

Fig. 7a and 7b show dramatically, in perspective view, the differences between the H_2 only reduction process, Fig. 7a, and the a.c. process, Fig. 7b, under what we believe to be very demanding conditions, i.e. with half of the wafer overcoated with oxide, and the other half bare silicon. In addition, the temperature was increased to 450℃ which, it is reported, tends to degrade selectivity [17]. The flow rates of the several gases was the same as before. The average thickness was 350nm,



a)

b)

Fig. 7 Surface characteristics of tungsten deposited on a half oxided silicon wafer using:
(a) H_2 rdduction
(b) a 30″/10″ a.c. cycle. Both are at 400℃, torr, 50sccm WF_6, 500 sccm H_2, 400 sccm Ar to a Thickness of 350 nm.

and a 30″/10″ sequence was used in the a.c. process.

Thus, we may conclude, that in a variety of oxide patterns, excellent selectivity is attainable under the conditions employed in an a.c. process up to thickness of at least 420nm, the maximum thickness deposited.

4.2 KINETIC ASPECTS OF THE A.C. PROCESS

To grow the approximately 350nm thick tungsten films via a 30″/10″ a.c. process at 450℃, (Fig. 7b) using the gas flows indicated, 27 cycles were required (a total of 1080 seconds elapsed time, i.e. 27×40″). This translates into an average growth rate of approximately 20nm/min referenced to the total elapsed time, and 26nm/min referenced to the deposition portion of the cycle (27×30″). At the same temperature, the growth rate in the H_2 only reduction process was approximately 40nm/min. This means that the etching portion of the cycle removed approximately 14 nm/min, of the tungsten, referenced to the depo-

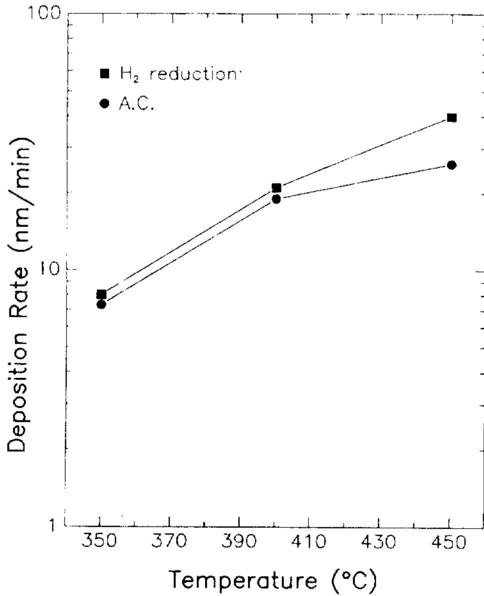


Fig. 8 Deposition rate (referenced to deposition time) vs. temperature for tungsten deposited under the pressure and flow conditions of Figure 7.

sition portion of the cycle at 450℃

This is an important consideration in choosing optimum conditions for STD. It was found at lower temperatures, 400℃ and 350℃, that the difference in growth rates between the H_2 only and a.c. processes(referenced to the actual time of deposition, as compared to the total elapsed time) is much less than at 450℃., as can be duduced from Fig. 8. Fig. 8 shows the growth rate as a function of temperature based on the deposition time only. Thus, in the H_2 reduction case the deposition time and the total elapsed time are identical. In an a.c. process, on the other hand, the deposition time is less than the total elapsed time. The results depicted in Fig. 8 imply that the increase in the kinetics of the ectching portion of the a.c. sequence with increasing temperature is greater than the increase in the deposition rate in the same temperature interval(its activation energy is greater). Consequently, for more than one reason(possible loss of selectivity being another), it is advantageous to conduct the a.c. process at as low a

Table 1 Comparison of AC. sequences at 400℃ , $WH_6+H_2+Ar=50+500+400$ Sccm, 1 torr

Cycle	H_2 reduction a	H_2 reduction b	30s/10s	30s/15s	30s/20s
Thickness, nm	340	425[4]	270	320	315
Deposition rate referenced to H_2 time in nm/min	21.0	19.0	20.0	20.0	21.0
Resistivity $\mu\Omega$cm	23.0	15.4	16.5	16.5	16.0
Seiectivity	VP[1]	VP[2]	VSL[2]	E[3]	E[3]

1. Very poor.
2. Very slight loss
3. Excellent.
4. $WF_s+H_2+A_r=50+2000+400$sccm

· Thickness of the tungsten films were determied using a surface profilometer and a SEM.

· Sheet resistance were measured with measured with a standard four point probe and resistivity calculated using the relation $\rho=R_s \cdot t$.

Table 2 Comparison of AC sequences at thicknesses around 400nm

Cycle	H_2	30s/10s	30s/15s
Thickness, nm	420	435	375
Resistivity $\mu\Omega$cm	15.4	15.7	16.9
Selectivity	Very poor	Excellent	Excellent

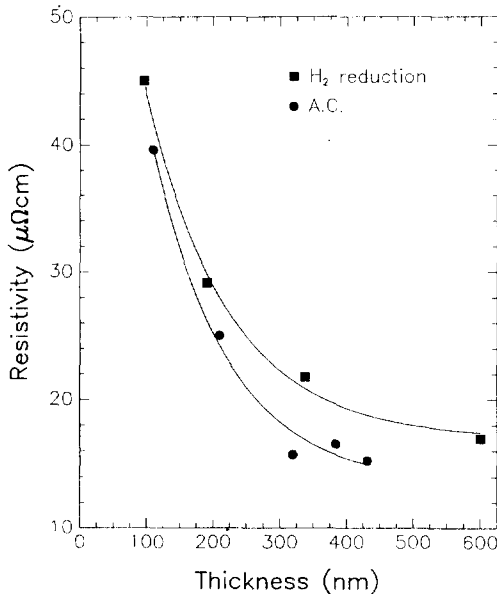


Fig. 9 Resistivity vs. film thickness for H_2 reduction and a.c. tungsten films deposited in a 30″/10″ Cycle under the pressure and flow condition of Figure 7.

tmperatuer as is practical. From Fig. 8 we see that at 400℃ and 350℃ the deposition rates in an H_2, and in an a.c. process, referenced to the deposition portion of the cycle are similar.

Table 1 gives a comparison, at 400℃ of the results of deposition experiments of three different a.c. sequences resulting in thicknesses of around 300nm. In the same table is given the results of a hydrogen reduction for the same thickness and flow conditions, as well as for a thicker H_2 deposited film used to determine the limiting resistivity in the appartus employed.

Table I is self explanatory for the most part. Note however, that the resistivity of the deposited films obtained, in the apparatus employed, by both the "conventional" hydrogen reduction, as well as by the a.c. method is about a factor of two greater than the bulk resistivity of pure tungsten. In general, the bulk value has not been reported as consequence of thin film tungsten deposition, a number more like 10-11 μΩ cm being more common.[16] In the second column under H_2 reduction in Table I, it is seen that for thicker tungsten films (grown at higher hydrogen flow rates than in our "standard"process) the value is only slightly better than obtained in the a.c. process. In general, it was found during the course of the present work that the resistivity obtained using the a.c. technique decreased with increasing thickness. This is depicted in Fig. 9 for a.c. films grown by the our standard process using a 30″/10″ sequence. It is seen that the resistivity appears to level off at about 400nm at a value of about 15μΩcm. This resistivity behavior is being investigated further.

One final comparison was made between a.c. sequences in 30″/10″, and 30″/15″ sequences, this time at thicknesses around 400nm using our standard conditions. A separate H_2 reduction run was conducted with which to compare these results, Table Ⅱ.

5. Conclusions

In summary, a new technique for achieving selective tungsten deposition has been shown to be effective to at least thicknesses of 400nm, with no obvious reason why it could not be employed to much thicker levels. This technique is termed an Alternating Cyclic, a.c., process, and involves the periodic interruption of the hydrogen redution of tungsten tetrahalide. During this periodic interruption, incipient(precursor) nuclei are brought into the vapor phase by the cold to hot disproportionation reaction involving the formation of the pentafluoride via the reaction of tungsten with the hexafluoride. Under proper conditions of system concentration, tempratuere and a.c. times for the periodic sequences, the growth rate is essentially the same as for a hydrogen reduction, referenced to the time of reduction.

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