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Recovery of Tungsten from the Exhaust of a Tungsten Chemical Vapor Deposition Tool

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An ETC DryScrub plasma scrubber has been successfully tested for the capturing and recovery of metallic tungsten from the exhaust of a W chemical vapor deposition (CVD) tool. The scrubber operation was completely transparent to the upstream CVD process. The WF_6 destruction removal efficiency of the scrubber was determined with a quadrupole mass spectrometer. The system had been tested with two different plasma frequencies: 100 and 40 kHz. With the 100 kHz frequency, the destruction efficiency of WF_6 reached an initial value of 98% at a nominal dissipated power of 1200 W. However, the layer of W deposited on the scrubber electrodes contained hydrates of tungsten oxides. Moreover, the destruction efficiency of WF_6 dropped to less than 70% after eight consecutively processed wafers ("memory effect"). Introducing an intermediate H_2 plasma treatment ensured a continuously high efficiency, and improved significantly the purity of the deposited W layer in the scrubber. With the 40 kHz power supply, the maximum efficiency reached is more than 99% from a nominal dissipated power of 1100 W on. The purity of the deposited W layer is high (>99%). No memory effect was observed. Successful marathon runs have been performed with each tested frequency.

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Chemical vapor deposition of tungsten (W-CVD) is a commonly used processing technique in the semiconductor industry. The efficiency of this deposition process however is low: as much as 75% of the source gas tungsten hexafluoride (WF_6) remains unused in the tool exhaust. To date, only destructive methods can be used to treat the waste gases, *e.g.*, burners and wet scrubbers. The disadvantage of these systems is that the waste gas stream is transferred to a wastewater stream. It is known that W-contaminated water is difficult to treat, due to the presence of multiple chemical states of W-containing species. No material is recovered or reused.

Environmental benign integrated circuit (IC) processing is becoming increasingly important. In addition, it is expected that the legislation on discharge limits will become more stringent in the future. The purpose of the work presented here is to assess the possibility of capturing and recovering (metallic) tungsten from the exhaust gas of a W-CVD tool in a dry way, using an ETC DryScrub plasma scrubber. By using this technique, a relatively large amount of the expensive W can be reused or sold which should make this treatment system economically feasible.

Experimental

Plasma scrubber.—The ETC DryScrub system is in essence a plasma enhanced (PE) CVD tool. Inside this scrubber, PE reactions can take place. Figure 1 displays a cross section of the scrubber. It contains two concentric spiral electrodes, labeled 3 and 4 [one grounded (anode) and one connected to the radio frequency (rf) feed-through (cathode)]. Three ceramic isolators (7) are used to separate the electrodes from each other. Both electrodes are placed in a grounded cylindrical Al inner housing (5), which is in turn surrounded by a vacuum-sealed outer housing (8). In this way, a plasma can be created between the electrodes. The rf power supply can have different output frequencies. Two frequencies have been tested in these experiments: 100 kHz ± 100 Hz and 40 kHz ± 40 Hz. Some scrubber operation parameters can be varied: power applied to the plasma, orientation of the electrodes, pressure in the scrubber, concentrations of gases coming into the scrubber, and electrode material. The electrodes are typically made of Al but are also available in Fe and stainless steel. The volume of the scrubber is about 40 L. The mean flow length of the gas through the system is about 1.4 m. The spacing between the spiral electrodes is 1.3 cm. The total electrode surface is 42,000 cm^2.

The scrubber already has been used successfully to treat exhaust gases of hot wall nitride deposition[1] and Si deposition[2] processes with conversion efficiencies of more than 95%. In the hot wall nitride deposition process treatment,[1] dichlorosilane is destroyed in the scrubber resulting in N_2, H_2, and ammonia as gaseous reaction products; the nonconductive materials ammonium chloride and silicon nitride are deposited on the scrubber electrodes. The Si deposition[2] treatment was performed with the ETC DryScrub system between the roots blower pump and the rotation vacuum pump.

Experimental setup.—The complete experimental setup is displayed in Fig. 2. The ETC DryScrub system is installed in bypass mode in the exhaust line of the W-CVD tool (type Applied Materials P5000). It has been set up in prepump position because at this location, the pressure is always lower than 10 Torr, which is the maximal allowable operating pressure for the ETC DryScrub system.

The upstream W-CVD deposition process cycle contains four major steps: (*i*) nucleation, (*ii*) via fill, (*iii*) purge, and (*iv*) chamber clean. During the nucleation step, H_2, SiH_4, and WF_6 are used as source gases (with Ar as carrier gas); only H_2 and WF_6 are used during the via fill. During the clean step consecutively a nitrogen trifluoride (NF_3) plasma and a H_2 plasma are applied. The wafer size used in this process was 150 mm. Typically a W layer of 1 μm was deposited on the wafer per process cycle.

During the via fill step of the W-CVD deposition, the total gas flow was 5600 standard cubic centimeters per minute (sccm) (Ar,

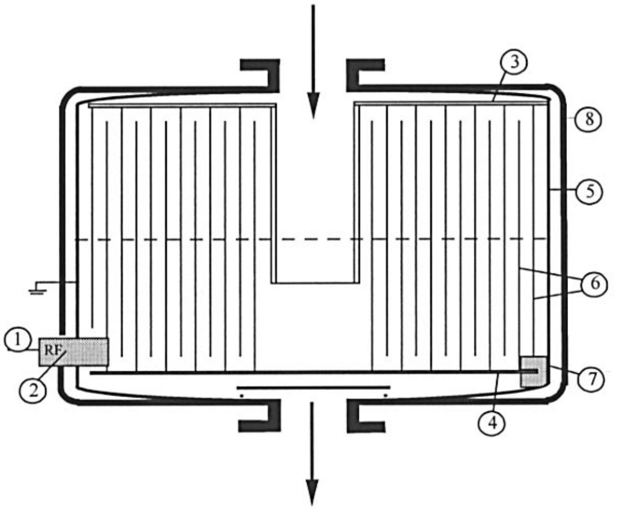

Figure 1. Cross section of the ETC DryScrub® system; 1: rf connector, 2: rf feed-through, 3: anode, 4: cathode, 5: inner housing, 6: spiral sets, 7: isolator, 8: outer housing.

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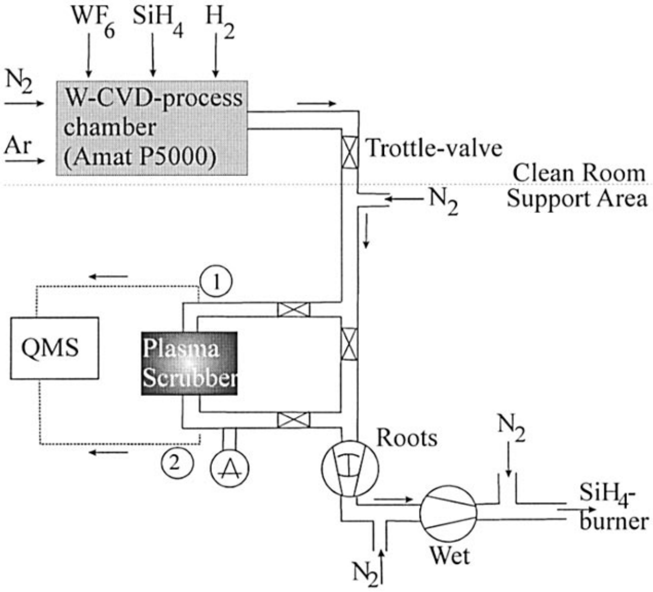

Figure 2. Schematic of the complete experimental setup.

N_2, H_2, and WF_6). The relative concentration of WF_6 in this gas mixture is only 1.34%. The mean residence time of the gases in the exhaust line is about 6 s; in the scrubber itself it is less than 1 s. Ideally, the recovered metallic tungsten should be as pure as possible. Therefore, only during the via fill step of the W-CVD process the plasma scrubber is activated. In this way, the codeposition of Si on the electrodes of the plasma scrubber is minimized.

A set of electropneumatic valves and a valve controller system make it possible to set the scrubber in bypass during the NF_3 chamber clean of the W-CVD chamber, preventing the removal of the deposited material on the scrubber electrodes. Another possibility is to switch the controller to the scrubber purge mode in order to be able to pump/purge the scrubber with pure N_2. It is also possible to add an additional gas (like H_2) to the scrubber inlet during the scrubber active operation (at position 1, Fig. 2).

The real-time, continuous gas analysis was carried out with a quadrupole mass spectrometer (QMS). A Balzers QMG-421, equipped with a differential pumping system, was used to sample at different pressure regions. This mass spectrometer allows quantitative as well as semiqualitative measurements. The sampling tubing is made of Teflon-like material because it has a higher resistance toward aggressive gases. It also reduces WF_6-metal catalyzed reactions. The sampling lines have a length of approximately 50 cm each, and an outer diam of 0.3 cm. Sampling can be done at the inlet and outlet of the plasma scrubber (at position 1 and 2, Fig. 2). The signals in the mass spectrometer are detected with a delay of about 15 s compared to the moment the gases are introduced in the upstream W-CVD chamber. The W-CVD tool is equipped with a dry roots blower pump with a capacity of 250 m^3/h and a wet rotation pump with Fomblin oil and a capacity of 65 m^3/h.

The pressure was monitored during the via fill deposition step on different locations throughout the setup. Pressure values were 80 Torr in the W-deposition tool, 1.5 Torr at the sample point before the scrubber (both measured with Baratron pressure gauges), and about 10^{-5} Torr in the mass spectrometer chamber (measured with a cold cathode pressure gauge). Over the scrubber, a pressure drop of 0.5 Torr was measured. The conductance of the exhaust piping, both without and with the scrubber, was calculated for air at a mean pressure of 2 Torr. The flow in the exhaust lines was in both cases in the laminar regime. A conductance of 11.212 m^3/s was calculated for the original piping before installing the scrubber, and a conductance of 0.025 m^3/s was obtained when the gases were going through the scrubber. This higher flow resistance prompted only an adjustment of the N_2 ballast at pump level. No other changes had to be made.

Results

Influence of the ETC DryScrub system on the W-CVD process.—A paramount requirement for the scrubber system is that it must be completely transparent to the upstream W-CVD process. Therefore, initial experiments have been performed to monitor the quality of the deposited W layer on the wafers during scrubber operation.

The pressure in the exhaust has been measured (at position 1, Fig. 2). As could be expected (see previous section), a 25% increase to 1.2 Torr was observed when the gases were led through the scrubber. About the same pressure was observed when the scrubber was active. This pressure increase however had no influence on the W-CVD process.

The weight and the resistivity of the deposited W layer on the wafers in the W-CVD tool during scrubber operation have been determined and were very well within the specifications needed. The standard deviation on the resistivity was very low: 0.64% of a resistivity value of 0.0962 $\Omega/\square$, indicating a very good uniformity of the deposited W layer on the wafer. The values were all comparable with the ones obtained before the installation of the scrubber. Particle addition was also investigated. No additional particles larger then 0.3 μm were generated using the ETC DryScrub system.

It can safely be concluded that the presence and operation of the ETC DryScrub system had no influence on the upstream deposition process in the W-CVD tool. Consequently, no process requalification is required upon installing the scrubber, given the currently used vacuum pump configuration.

Gas stream analysis.—A mass spectrometric analysis of the gases present in the exhaust was performed with the Balzers QMS. All measurements were done using an ionization energy of 40 eV to avoid the creation of too many double ionized species in the analyzer. Secondary electron multiplier detection was used for sensitivity reasons.

On the mass spectra obtained during processing, one could easily assign some peaks to the products of the reactions occurring in the W-CVD tool, as well as to the various products of the plasma process occurring in the scrubber. The most prominent peaks are those coming from the source gases WF_6, H_2, and SiH_4. In addition, HF/F, WO_3, and WOF_4 could be identified as the most important byproducts. Evidence for the presence of minor amounts of air and moisture in the dry scrubber itself were found as well.

Since W has isotopes at masses 182 [relative abundance (R.A.), 26.3%], 183 (R.A., 4.3%), 184 (R.A., 30.7%), and 186 (R.A., 28.6%), a complex mass spectrum is obtained when measuring the effluent stream. Therefore, a lot of attention went to the correct identification and assignment of the individual mass peaks. Since the parent ion WF_6^+ does not exist, WF_5^+ was found to be the most important fragment of WF_6 after electron impact dissociation and ionization at 40 eV. This was confirmed by the National Institute of Standards and Technology reference mass spectrum at 70 eV.[3] Therefore, the highest isotope peak of the WF_5^+ fragment (mass 279), has been selected to monitor WF_6. Moreover, this mass does not interfere with a peak of WOF_3^+, the largest fragment of WOF_4. When other fragments of WF_6 were monitored, mass peaks were always chosen in such a way that no mass interference of other species was present. Table I gives a concise overview of possible species present with corresponding masses.

A linear calibration curve of WF_6 over four concentration decades was obtained. The detection limit of WF_6 was about 5 ppm. Figure 3 displays a time resolved spectrum of the representative peaks of H_2 (mass, 2), HF (mass, 20), SiH_4 (mass, 30), and WF_6 (mass, 279) during consecutive nucleation, via fill, and purge steps of the W-CVD process. Sampling was done here at the scrubber outlet (position 2, Fig. 2). The different masses were measured with different QMS sensitivities. The two measurement conditions are (A) scrubber not active and (B) scrubber active.

Figure 4 gives an overview of the ion intensities obtained for the most important peaks during the via fill step of the deposition for

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Table I. Mass peaks interpretation table.

Mass number (amu)	Species
281, 279	WF_5^+
278	WF_5^+ and WOF_4^+
277	WF_5^+
276, 275,274	WOF_4^+
262, 260	WF_4^+
259	WOF_3^+ and WF_4^+
258	WF_4^+
257, 256, 255	WOF_3^+
243, 241	WF_3^+
240	WF_3^+ and WOF_2^+
239	WF_3^+
238, 237, 236	WOF_2^+
224, 223	WF_2^+

both scrubber active and scrubber not active conditions (sampled at position 2, Fig. 2).

Determination of the WF_6 destruction efficiency.—An important property regarding the scrubber performance is the destruction removal efficiency (DRE) of WF_6. It is defined by the formula

$$WF_6 \text{ DRE} = \left(1 - \frac{i_{\text{M279,scrubber active}}}{i_{\text{M279,scrubber not active}}}\right) \times 100 \qquad [1]$$

The *i* in the equation denotes the area under the time resolved intensity of mass 279 during the via fill step (see Fig. 3). The uncertainty on the efficiency values is ±1% absolute.

The DRE of the scrubber is sensitive to several parameters. Some of them can be changed, others are more or less fixed in the setup presently used. An important parameter is the frequency of the plasma generator. The results reported below are grouped as function of two frequencies which have been tested: 100 and 40 kHz.

Results with the 100 kHz plasma frequency.—Dissociation efficiency optimization.—The scrubber performance is very sensitive to the dissipated power to the plasma. The WF_6 DRE of the scrubber is increasing with increasing power (see Fig. 5). Initial experiments were done with an Al electrode. Since the maximum applicable power using the Al electrode was limited to 800 W, further experiments were done with an Fe electrode. The maximum power that could be applied here was 1200 W (power density, 0.06 W/cm^2). It has to be noted that no information could be obtained about the amount of power reflected from the electrodes. Consequently, all power-values mentioned in this article are "nominal".

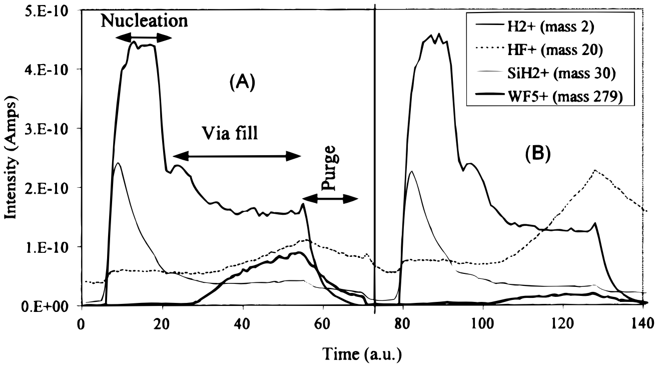

Figure 3. Time resolved mass spectrum during nucleation, via fill, and purge steps of the W-CVD process with the scrubber not active (A) and with the scrubber active (B) for several representative peaks, sampled at the scrubber outlet.

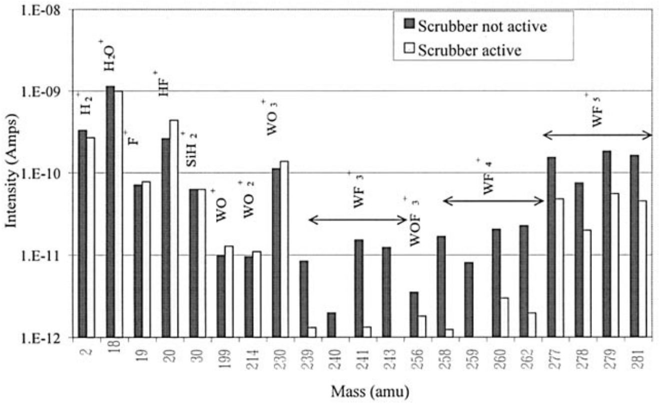

Figure 4. Ion intensities of selected masses for two conditions, scrubber active and scrubber not active, sampled at the scrubber outlet.

Another determining parameter for the DRE is the total pressure in the scrubber. Typically, the pressure in the exhaust line of the CVD tool during processing is about 1 Torr, staying well below the recommended operating pressure for the scrubber of 10 Torr. Changing the pressure in the scrubber to lower values could have a positive effect on the scrubber efficiency. However, this could not be verified since the minimum pressure in the exhaust line is fixed by the upstream W-CVD process and the limited capacity of the downstream vacuum pump. Increasing the pressure by adding additional carrier gas to the exhaust stream resulted in lower efficiencies.

Tests have shown that the $[WF_6]/[H_2]$ ratio in the exhaust also influences significantly the WF_6 DRE of the scrubber. The smaller the ratio is, the higher the efficiency will be. However, in normal conditions, this ratio is determined by the upstream W-CVD process and cannot be changed ($[WF_6]/[H_2] \approx 0.15$). Adding up to 4 standard liters per minute (slpm) forming gas (10% H_2 in N_2) directly to the scrubber inlet (at location 1 in Fig. 2) during scrubber operation in order to decrease the mixing ratio, causes a decrease of the scrubber efficiency. The positive effect of increasing the $[H_2]$ is suppressed here by the negative effect of the pressure increase.

Initial experiments showed that the orientation of the electrodes in the scrubber had also an effect on the WF_6 DRE of the scrubber. The destruction efficiency was about 10% lower when the gases were flowing from the outside of the electrode to the inside, than when the flow was from the inside to the outside. No clear explanation could be found for this observation, but it is certainly related to the asymmetric radial distribution of the plasma between the electrodes. In the experiments described below, Fe electrodes with inside to outside orientation and a nominal dissipated power of 1200 W have been used.

Amount of W that can be recovered.—Given the total inlet flow of WF_6 process gas and the amount of W deposited on the wafer in the

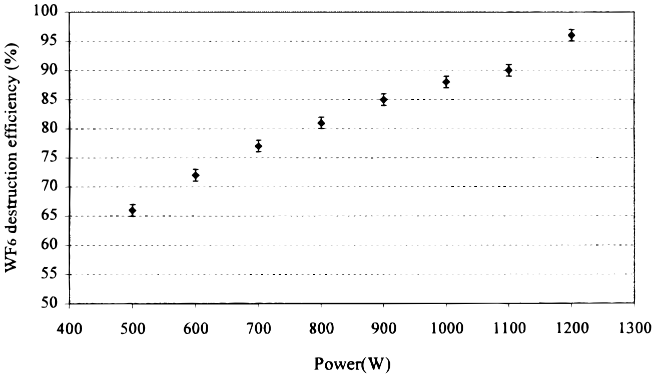

Figure 5. WF_6 destruction efficiency as a function of dissipated power given to the plasma (100 kHz power supply experiments).

upstream CVD process, the maximum amount of W that can be deposited on the scrubber electrodes can be calculated. Theoretically, with a DRE of 99%, about 1.8 g pure W per W-CVD cycle can be deposited on the electrodes. An amount of 1.9 g deposit has been found on the electrodes, indicating that the layer is not pure W.

Quality of the deposited W layer.—The quality of the deposited W layer on the scrubber electrodes, obtained after about 350 deposition cycles with the above described optimized process parameters, is not satisfactory. The layer has a deep blue color and thus is not made of pure metallic W. The crystals obtained were identified by X-ray diffraction (XRD) analysis as $H_xWO_3 \cdot yH_2O$, a form of tungsten blue, one of the products of the oxidation of W with moisture (see the Discussion section). In addition, a significant concentration of F-containing species was present in these crystals. Total reflection X-ray fluorescence spectrometry (T-XRF) analysis of the layer could not detect the presence of other metals. Microscopic inspection revealed that the deposit is made of several individual layers on top of each other. Furthermore, it can be seen that the coverage of the electrodes is local and not homogeneous.

Memory effect and intermediate H_2 plasma treatment.—Using the optimized conditions, an initial WF_6 DRE of approx. 99% was reached. However, it was found that the within batch efficiency decreased with each consecutive wafer processed in the W-CVD tool. As can be seen on Fig. 6 (data set of no H_2 plasma treatment), after processing of eight wafers, the efficiency dropped to only 81%.

In order to cope with this memory effect and to improve the efficiency of the scrubber, an H_2 plasma treatment of the electrodes was introduced after each wafer processed. Moreover, this should result in an improved quality of the deposited layer. The justification for this H_2 plasma treatment introduction can be found in the Discussion section.

This intermediate H_2 treatment consists of striking a plasma in the scrubber at the same nominal power used during the deposition step of the process, while flowing H_2 gas and some additional carrier gas (Ar) through the scrubber. The H_2 comes from the upstream W-CVD chamber, where it is used during the cleaning of the deposition chamber. During this step, the pressure in the scrubber is <1 Torr. Initial experiments using this intermediate H_2 treatment demonstrated that it was indeed effective in regaining a WF_6 destruction efficiency of more than 97%, after an initial small dip. Figure 6 displays the WF_6 DRE of a run where an H_2 plasma treatment is applied of 1 slpm for 120 s.

Investigations have been carried out to optimize the conditions of this H_2 treatment by defining the optimal H_2 flow rate and flow time. Since the introduction of the H_2 treatment has a negative effect on the process throughput of the W-CVD tool, the time necessary for the treatment should be as short as possible. Figure 7 gives an overview of WF_6 DRE results for several H_2 treatment conditions (with data obtained each time at the ninth wafer of a batch, thus well after the initial dip). The most optimal treatment is a trade off between the H_2 gas consumption and the time necessary (or available) to perform the treatment.

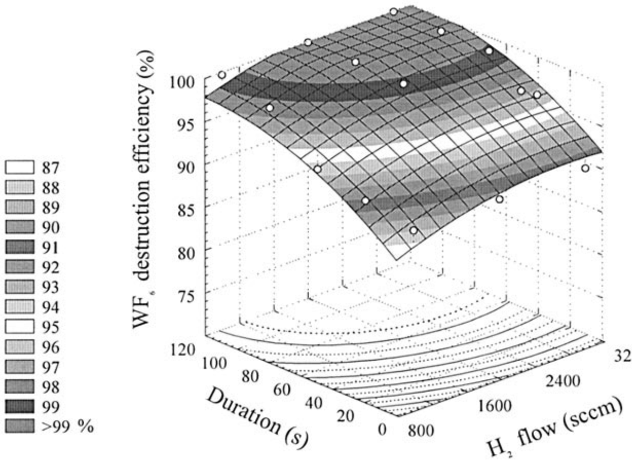

Figure 7. Optimization tests of the intermediate H_2 plasma treatment as function of duration and H_2 flow. Data always taken at the ninth wafer of a batch (100 kHz power supply experiments).

A marathon run has been performed using this intermediate H_2 treatment. As can be seen on Fig. 8, after an initial dip, a continuous WF_6 destruction efficiency of ≥98% is achieved. Visual inspection of the deposited W-containing layer on the scrubber electrodes revealed that the quality obtained when using an intermediate H_2 treatment is very different from the deposited layer obtained when no H_2 treatment was used. The layer has now a homogeneous metallic color and is homogeneous in structure as well. The coverage on the electrode is complete and seems to be uniform over all the electrode surface. Only the layer in the region near the rf feed-through is bluish, indicating the presence of $WO_x \cdot yH_2O$. T-XRF and XRD analysis revealed that the layer on the electrodes consists of pure W, of both crystalline and amorphous phases. No evidence was found for the presence of other metals.

Results with the 40 kHz power supply.—The same experimental setup was used as with the 100 kHz experiments (see Fig. 2). The installation of this plasma power supply required only an additional water cooling circuit. The WF_6 DRE was also determined by measuring time-resolved mass signals with the Balzers mass spectrometer.

As in the 100 kHz experiments, Fe electrodes with inside to outside orientation have been used at an operation pressure of 2 Torr.

WF_6 destruction efficiency.—The influence of the dissipated power on the WF_6 DRE has been assessed. Again, the scrubber efficiency

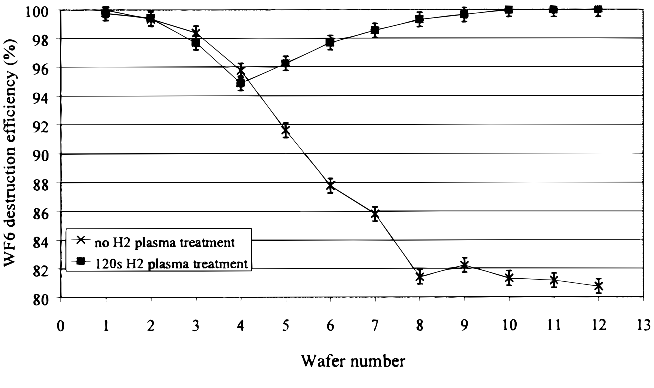

Figure 6. Comparison of the WF_6 destruction efficiency as function of wafer number without and with intermediate H_2 plasma treatment. Pressure during H_2 treatment was 0.7 Torr with a H_2 flow of 1000 sccm (100 kHz power supply experiments).

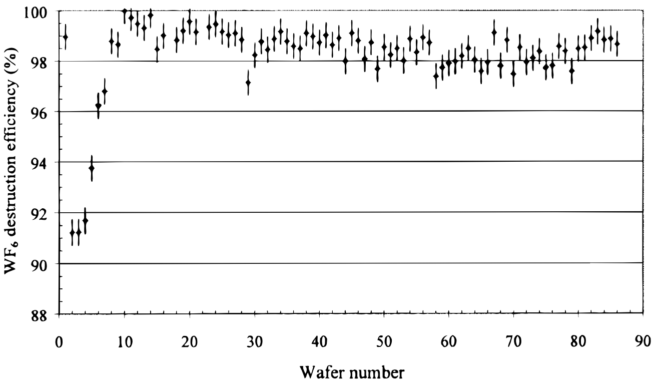

Figure 8. WF_6 destruction efficiency as function of wafer number during a marathon run, performed with the 100 kHz power supply and with an intermediate H_2 treatment of 120 s.

is increasing with increasing dissipated power. The minimum nominal dissipated power that has to be applied to obtain an efficiency ≥99% is about 1100 W. As opposed to the experiments with the 100 kHz power supply, no memory effect has been observed.

A marathon run has been performed with a plasma power of 2500 W. The results are displayed in Fig. 9. As can be expected, the WF_6 DRE is never lower than 99% during the complete run. No overheating of the system has been observed, although the temperature of the electrodes was about 70°C, which is 20°C higher than in the case of the 100 kHz power supply.

Resulting deposited W-layer.—The quality of the deposited layer obtained with the 40 kHz power supply is very good. It has a metallic tungsten-like appearance, and seems to be very homogeneous in structure and color. The coverage of the electrodes is complete and uniform over all the electrode surface. No blue deposits have been observed. No other metals besides W could be found with T-XRF analysis. From this it was concluded that the purity of the layer is very high.

Discussion

In the upstream WCVD tool, the deposition chemistries are SiH_4/WF_6 and H_2/WF_6-based. Silane and H_2 act as reducing agents for the tungsten source. The main corresponding overall reaction equations can be written as

$$WF_6 + 3H_{2(g)} \rightarrow W_{(s)} + 6HF_{(g)} \qquad [2]$$

$$2WF_6 + 3SiH_{4(g)} \rightarrow 2W_{(s)} + 3SiF_{4(g)} + 6H_{2(g)} \qquad [3]$$

Both reactions are thermally activated and proceed only at an acceptable rate at higher temperatures (>300°C). Reaction Eq. 3 is thermodynamically more favorable. Moreover, Reaction Eq. 2 is catalyzed by a metallic substrate.

An alternative (nonthermal) activation technique to deposit tungsten is by means of a gas discharge plasma[4,5] (*i.e.,* PECVD), which is also applied in the DryScrub system. Besides WF_x (with $1 \leq x \leq 5$) fragments and corresponding F radicals and F ions, the rf plasma in the scrubber also produces atomic hydrogen

$$H_{2(g)} + e^- \rightarrow 2H^{\bullet}_{(g)} + e^- \qquad [4]$$

which diffuses to the surface and reacts there in several consecutive steps with WF_x fragments to form metallic W and HF (apparent activation energy is ~39 kJ/mol). Experiments described in literature[6] are done at elevated substrate temperature (350°C) and at pressures around 200 mTorr. The electrodes were powered at a frequency of 4.5 MHz. Power densities are ~0.06 W/cm^2. The DryScrub experiments described in present article are executed at distinctively different conditions of 100°C and 1.5 Torr. Power densities are ranging from 0.04 to 0.25 W/cm^2 at plasma frequencies in the kHz region.

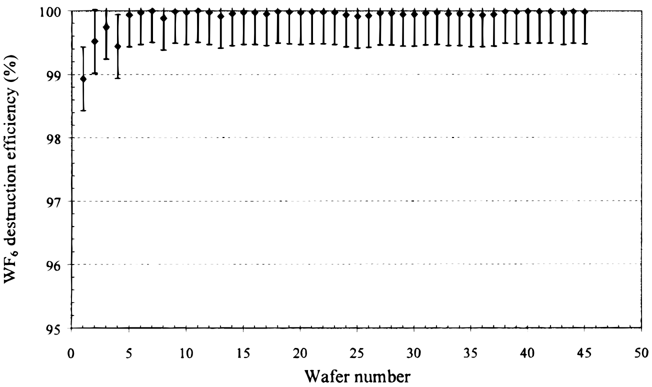

Figure 9. WF_6 destruction efficiency as function of wafer number during a marathon run, performed with the 40 kHz power supply. No intermediate H_2 treatment is used.

The chemistry becomes more complex when introducing moisture and/or oxygen in the system, coming from air leaks and degassing processes. There exist a variety of WOHF compounds in different ratios of oxidation states, each with its own physical characteristics. Among them the most important is WO_3, formed in Reaction Eq. 5 as final oxidation product (taking place preferably at the surface)

$$WF_6 + 3H_2O_{(g)} \rightarrow WO_{3(s)} + 6HF_{(g)} \qquad [5]$$

A stoichiometric composition of tungsten trioxide is yellow. However, a very common form of tungsten oxides are the tungsten blues, which are mixed valence compounds containing different ratios W(VI)/W(V) (*e.g.,* $H_{0.1}WO_3$, and the corresponding hydrate $H_{0.1}WO_3 \cdot 1.06H_2O$). It is reported that wet WO_3 becomes blue on exposure to ultraviolet light (*e.g.,* from the plasma emission) as a result of formation of tungsten blue.[7]

WO_3 can react with WF_6 [8]

$$WO_{3(s)} + 2WF_{6(g)} \rightarrow 3WOF_{4(s,g)} \qquad [6]$$

WOF_4 (tungsten oxyfluoride) in pure form is white, but in practice it is usually contaminated with other tungsten oxides, which can give it different colors (blue-yellow). It is known that those tungsten oxides may cause reduced deposition of W, poor morphology, and uneven growth. WOF_4 has a vapor pressure of about 1 Torr at 21°C, and can participate in the PECVD reactions. When it is oxidized (*e.g.,* by the introduction of air), the volatile WOF_4 is converted to WO_3 and tungsten blues which stay on the wall of the reactor.

As described earlier, during the scrubber experiments at 100 kHz without intermediate H_2 treatment, mass spectrometric WO_3 signals are observed. They increased as a function of lifetime of the electrode. However, at the same time, only trace amounts of WOF_4 (WOF_3^+ ion) could be detected. Also, when opening the scrubber for visual inspection, the deposited layer exhibits a variety of colors, ranging from metallic gray, over yellow to blue. The smell of HF upon opening of the scrubber was observed and cracking of the deposited layer was heard.

Regarding the chemical processes occurring in the ETC DryScrub system, it can be concluded that the WF_6 DRE is mainly dependent on the H_2 dissociation efficiency, and thus on the absolute concentration of H radicals ($H^{\bullet}$) and ions in the plasma. As described above, the H_2 concentration, the total pressure, and the plasma power density play a determining role toward the H radical formation, but could hardly be optimized in the present setup. The only [H]-determining parameter left which can be modified is the so-called surface condition of the electrodes. It influences the overall H_2 dissociation efficiency by catalyzing the surface $H^{\bullet}$ termination reactions like

$$H^{\bullet}_{(ad)} + H^{\bullet}_{(ad)} \rightarrow H_2 \qquad [7]$$

$$H^{\bullet}_{(ad)} + F^{\bullet}_{(ad)} \rightarrow HF \qquad [8]$$

and

$$H^{+}_{(ad)} + F^{-}_{(ad)} \rightarrow HF \qquad [9]$$

The electrode surface conditions are determined by the possible (pre-) treatment of the electrodes, and by the kind of deposits on the electrodes (see previous paragraph). The ideal deposit consists of pure W, not poisoned with any form of tungsten oxides. This can be achieved by making the complete prepump exhaust system as gastight as possible and by degassing the scrubber (bakeout) before operation, in order to minimize the presence of moisture and oxygen. On the other hand, reduction of tungsten oxides, already present on the electrodes, to metallic W is possible by treating the oxides in a H_2 plasma. The corresponding overall reaction is

$$WO_{3(s)} + 6H^{\bullet} \rightarrow W_{(s)} + 3H_2O_{(g)} \qquad [10]$$

Of course, the water vapor must be pumped off. Treatment with H_2 gas (without plasma) is only effective at temperatures >900°C. Moreover, an additional advantage of a H_2 plasma is that via Reac-

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tion Eq. 8 and 9, the adsorbed F atoms will be removed from the surface. When the scrubber is active over a longer period (>5 min) or at higher effective plasma powers, the increased temperature of the electrodes will also increase desorption of F.

The observed memory effect during continuous scrubber operation at 100 kHz is thus determined by the scrubber electrode surface condition, and can have several causes. One is the continuous buildup of WOF_4 (following Reaction Eq. 6), resulting in a decrease of the H_2 dissociation efficiency. Prevention of WOF_4 buildup was described previously. Another cause can be the buildup of F^- ions on the electrode surface. F^- ions are very stable in the gas phase ($\Delta H_{298} = -61$ kcal/mol) due to the high electronegativity of F. This may result in a shielding of the plasma.

In the same framework, the effect of the initial condition of the electrode surface of the scrubber can be understood. It was found that the WF_6 DRE during processing of the first six to seven wafers of a batch, can differ from batch to batch. This was related to the surface condition of the electrodes before processing. When the treatment preceding processing was an H_2 plasma, the initial WF_6 destruction efficiency was up to 6% higher than in the case where the initial treatment was a simple WF_6 flow (without plasma).

Note also that several analogous tests for destruction of NF_3 in a plasma reactor exhibited low efficiencies.[9] A potential solution could again be the use of an additional remote upstream H_2 discharge to treat the surface of the plasma scrubber. This prevents buildup of fluorine in the scrubber.

The better performance of the 40 kHz plasma power supply can tentatively be explained by the fact that, at this lower frequency, there is a higher probability of electron loss to the scrubber electrodes. Although the loss of negative ions (mainly the F^- species present in the plasma) may not be affected, it is expected that the absolute F^- concentration will also be lower. The overall plasma then becomes more positive since the shielding effect of F^- decreases. Therefore, the positive ion energy will become higher and the resistance heating of the electrode will increase accordingly. In addition, the maximum deliverable power will be higher. These benefits would result in a higher dissociation efficiency of H_2 and WF_6. On the other side, the hotter electrode helps the rf adsorption and the higher bias positive ions enhance the outgassing, the quality of the deposit and the reaction rate of the gases in the plasma.

At the plasma power frequencies of 40 and 100 kHz (including in the latter case an intermediate hydrogen plasma treatment), a high quality W-layer on the scrubber electrodes is obtained. However, pure W has good conductive properties. Therefore, the deposited layer can cause short circuiting between the plasma electrodes. The electrodes are isolated from each other by three ceramic isolators which are also in contact with the exhaust gases. The isolators can become covered by a tungsten layer as a function of processing time, thus creating a conductive path causing short circuiting between the electrodes. This results in a malfunctioning of the scrubber. This phenomenon occurs already after processing of a few hundreds of wafers.

In principle, this arcing could be suppressed by using a lower operating pressure in the scrubber or by lowering the electrode temperature. However, both these parameters are more or less fixed in the present test conditions. A preferable and more thorough solution exists in redesigning the plasma electrodes and isolators.

An additional issue that needs attention is the removal of the deposit from the electrodes in order to recuperate the metallic W. The bulk of the deposited W can be removed mechanically and collected very easily. If necessary, it can even be scraped off manually. The remaining part can be dissolved in a solvent to remove it from the electrode surface. Metallic W can be dissolved in an ammonium hydroxide solution. The blue tungsten oxide compounds can be removed by a hydrogen peroxide solution.[9] After the complete removal of the deposits, the electrodes can be reused in the scrubber.

For reasons of completeness, it should be mentioned that some safety precautions should be taken during handling of the electrode after processing. It is recommended to wear skin and respiratory protection, since some W-O(-F) compounds are irritating and/or toxic.

Conclusions

It has successfully been demonstrated that it is possible to capture and recover pure W from the exhaust of the W-CVD tool by means of a commercially available ETC DryScrub system. Two different frequencies of the plasma power supply have been tested: 100 and 40 kHz. With the 100 kHz frequency, an initial WF_6 DRE of 98% has been obtained at a nominal dissipated power of 1200 W. However, a memory effect has been observed, causing the DRE to drop from 98% to less than 70% after eight consecutively processed wafers. This memory effect is believed to be caused by a continuous buildup of F^- ions in the scrubber. Under these conditions, the resulting deposited W layer on the scrubber electrodes is of poor chemical and physical quality. The memory effect has been resolved by using an intermediate H_2 plasma treatment of the scrubber, resulting in a continuous WF_6 destruction efficiencies of at least 99%. The introduction of the H_2 treatment resulted also to an excellent deposited W layer on the scrubber electrodes.

With the 40 kHz plasma frequency experiments, a continuous WF_6 DRE efficiency of more than 99% has been reached with a nominal plasma power of 1100 W or higher. No memory effect has been observed and consequently no intermediate H_2 treatment was necessary. The quality of the deposited layer was very good and was identified as pure W. No evidence was found of other metals within the deposit.

Regarding the implementation of the scrubber in an industrial environment, the following can be concluded: The scrubber operation itself was found to be completely transparent to the upstream CVD process. No additional gasses are needed to operate the scrubber. Both plasma frequencies tested (100 and 40 kHz) can be used. Preference however should go to the lowest frequency for reasons of throughput and gas consumption. The deposited W in the scrubber can easily be recuperated. The problem with the limited lifetime of the scrubber electrode due to arcing is still an issue that is subject for improvement.

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