Evaluation of the Selective Tungsten Deposition Process for VLSI Circuit Applications

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ABSTRACT

Tungsten films have been selectively deposited on oxide-patterned silicon wafers using two successive deposition steps, *i.e.*, the Si reduction of WF_6 followed by the H₂ reduction of WF_6 . The deposition process was performed in a horizontal hot wall LPCVD reactor. In this reactor, the surface of vertical wafers was parallel to the axis of the quartz tube. The thickness of W films obtained for a given deposition time was found to be dependent on the "history" (or the cleanliness) of the CVD reactor. The thickness uniformity across a wafer and from wafer to wafer was determined as a function of the wafer position in the CVD reactor. The selectivity of the process was evaluated by measuring the W nuclei density on the oxide (PSG) mask as a function of the thickness of W films. During the validity period of the CVD reactor, tungsten films of 220 nm in thickness were produced on 12 wafers per run with undetectable W nuclei on the mask (perfect selectivity). The CVD reactor appears to be suitable for selective deposition of W films used as diffusion barriers in Al/W/Si contact structures.

During the last few years, continuous interest has been shown in the selective low pressure chemical vapor deposition (LPCVD) of tungsten films for metallization of very large-scale integrated (VLSI) circuits (1). Among many promising applications of the W deposition process, the use of selective W films for contact and diffusion barriers between aluminum and silicon appears to be a very attractive metallization scheme (2). Tungsten hexafluoridehydrogen mixtures are currently used as starting materials in the selective W deposition. The growth of W films on areas of bare silicon distributed over oxide-patterned silicon wafers starts with the Si reduction of WF_6 , in spite of the presence of hydrogen in the gas phase, and this reduction reaction proceeds rapidly until a W thickness limit is reached (3). Once this limited layer is deposited, W films continue to grow by the H_2 reduction of WF₆. The deposition rate of W films produced by the Si reduction of WF₆ (first deposition step), as well as the metal thickness and consumption of silicon substrates, can be difficult to control. The thicknesses of the W films and of the Si consumed have been found to be dependent on the crystal perfection of the Si substrates (4), the native oxide thickness on the Si surface (5), and the implant dose and type of dopant in the contact areas (2). During this first deposition step, various other problems can appear, such as encroachment of the tungsten at the Si-SiO₂ interface (haloing effect), tunnel formation in the silicon (wormholes), and preferential erosion of the As-doped n⁺ contact areas as opposed to the Bdoped contact areas (2). Following this first deposition stage, the growth of W films occurs by the H₂ reduction of WF₆. After several successive deposition runs performed in the LPCVD reactor, the quartz tube, quartz boat, and oxidized dummy wafers are covered with a W deposit, and the deposition rate of selective W films decreases significantly (6). This dependence of the deposition rate on the "cleanliness" of the quartzware leads to a poor reproducibility of the thickness of W films produced for a given deposition time. Although these reproducibility problems in the selective W deposition process using either hot wall (7) or cold wall reactors (8) are known to exist, they are not clearly discussed in the literature. Also, various crucial features of the selective W deposition by the H₂ reduction of WF_6 , such as the uniformity of W thickness and wafer throughput, have not yet been reported. However, these experimental characteristics are of great interest when using this process in the manufacturing of VLSI circuits.

In the present study, W films are selectively deposited on oxide-patterned Si wafers using a two step deposition process under fixed experimental conditions (substrate temperature and composition of reactant gas mixture). The W thickness is measured as a function of the deposition time in order to investigate the reproducibility of the CVD process. The thickness uniformity of W films within a wafer is investigated as a function of the position of wafers in the CVD reactor. The experimental data on the selectivity of the process obtained by measuring the density of W nuclei on the SiO_2 surface are also presented in this paper.

Experimental Method

The substrates consisted of (100)-oriented single-crystal Si wafers, with a p- or n-type conductivity, a resistivity of 20-40 Ω -cm, and a diameter of 100 mm. The Si wafers were covered with a 25 nm thick thermal oxide layer and received either an As⁺ or B⁺ ion implantation. The implant energy and dose are given in Table I. These ion-implanted wafers were coated with a 500-600 nm thick phosphosilicate glass (PSG) layer deposited by LPCVD at 430°C. After densification of the PSG layer by annealing at 650°C for 30 min, the As and B implants were activated by rapid thermal processing. The values of junction depth, sheet resistance, and surface doping concentration listed in Table I were calculated by simulation of the processing conditions. The test pattern for selective W deposition (Fig. 1) delineated by standard photolithographic methods consists of a network of 200 μ m wide perpendicular strips delimiting 48 squares. Within each square, 16 windows of various sizes (600, 400, 200, and 100 μ m) are opened by reactive ion etching. The total surface area for selective W deposition on each wafer is about 3 cm². After photoresist stripping, the test wafers were cleaned in a mixture of (2.5:1) H₂SO₄:H₂O₂ for 15 min, rinsed in deionized water, and nitrogen spin dried before storage in dustproof containers.

Prior to the metal deposition, the test wafers were etched in a (10:1) HF solution for 20s to remove the native oxide layer on the Si regions, rinsed in deionized water, and nitrogen spin dried. These wafers and thermally oxidized dummy wafers were then placed in the quartz boat and immediately loaded into the reactor. The quartz boat contained 8 rows (A to H) of 10 wafers (Fig. 2). The batch size of the CVD reactor was 12 test wafers per run. The CVD system has been described in detail in a previous paper (6). The W films were deposited at 285°C via two successive deposition steps. During the first deposition step, only WF_6 and argon used as a carrier gas were injected into the reactor for a few minutes. The flow rates of WF₆ and Ar were 20 and 750 cm³/min and the partial pressures of these gases were 3 and 200 mtorr, respectively. About 15 nm thick W films were grown on the test wafers via the Si reduction of WF₆. After this first deposition step, the reactor was purged by a pure argon stream for 2 min and, then, during the second deposition step, the growth of W films proceeded via the H_2 reduction of WF_6 . The flow rate and partial pressure of WF₆ were 90 cm³/min and 16 mtorr, respectively. These deposition experiments were performed at an H₂ partial pressure of 700 and 350 mtorr corresponding to an H₂ flow rate of 3.75 and 1.86 l/min, respectively. The flow rate of argon was adjusted to maintain the total pressure at 1.4 torr. The total flow rate of the gas mixture

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Table I. Values calculated by simulation of the processing conditions

| Implant | Dose (cm ⁻²) | Energy (keV) | Junction depth (µm) | Sheet resistance (Ω/sq) | Surface doping concentration (cm ⁻³) |
|---------------------------------------|-------------------------------------|-----------------|---------------------------|-------------------------------|--|
| \mathbf{B}^{*} \mathbf{As}^{+} | $2 	imes 10^{15} \ 4 	imes 10^{15}$ | 30 130 | 0.57 0.25 | 60 34.6 | $9.5	imes 10^{19}\ 2.9	imes 10^{20}$ |

was about 75 l/min. After a series of deposition experiments, the quartz tube and boat were cleaned by dipping in a $\rm HNO_3$ -HF solution.

After W deposition, the wafers were partially covered with a wax mask, and tungsten steps were etched in 200 µm wide stripes by dipping the samples into a ferricyanide solution (9). The thickness of the W films was measured in zones 1 to 9 of each test wafer (Fig. 2) by using a stylus profilometer and the mean thickness in each zone was calculated to determine the reproducibility of the process as well as the film thickness uniformity across a wafer, from wafer-to-wafer and from run-to-run. To evaluate the selectivity of the CVD process, the density of W nuclei on the oxide mask was determined on the test wafers and on the thermally oxidized dummy wafers positioned in lane 4, i.e., opposite to the test wafers. The number of W nuclei on test wafers was counted within areas of 2500 µm² in the center of the wafers (zone 5) using an optical microscope at a magnification of 1000. The density of W nuclei grown on dummy wafers was determined within a surface area of 15,000 μ m² by viewing the sample with an optical microscope coupled to an image analyzer. The number of nuclei was counted at different positions 0.5 cm apart along a diameter of the dummy wafers which was parallel to the horizontal axis of the quartz tube during deposition of the W films.



Fig. 1. Test pattern for selective deposition of W films on Si wafers. Si (dark areas); SiO₂ (light areas); square windows of different sizes (600, 400, 200, and 100 μ m).

Experimental Results

Growth kinetics of selective tungsten films.-The Si reduction of WF₆ leads to the formation of about 15 nm thick W films with a good reproducibility regardless of the deposition conditions investigated. As the deposition runs proceed, the surface of quartz tube, boat, and oxidized dummy wafers are progressively covered with W nuclei. The deposition rate of W films produced by the H₂ reduction of WF₆ appears to be affected by the density of W nuclei on the quartz surface, i.e., by the "cleanliness" of the CVD reactor. To investigate the effect of the cleanliness of the quartzware on the reproducibility of the selective W deposition via the H_2 reduction of WF_6 , the thickness of W films in the center of the test wafers positioned in rows C, D, and E was determined as a function of the deposition time for the series of experiments carried out at an H₂ partial pressure of 700 and 350 mtorr (Fig. 3). The film thickness given in Fig. 3 is obtained after deduction of 15 nm from the total W thickness determined by stylus profilometer measurements, and the deposition time is the duration of the second deposition step (H_2 reduction of WF_6).

The W thickness obtained by the H_2 reduction of WF₆ for a given deposition time between two cleaning sequences of the CVD reactor varies with the cleanliness of the quartzware. Three different periods can be distinguished in the evolution of the CVD reactor. Just after cleaning of the quartz tube and boat, the deposition rate of the films is negligible or very low and increases progressively as the deposition time increases. This first period, or "stabilization period," of the CVD reactor can be as long as 2 or 3h. Beyond this period of time, the thickness of W films produced by successive runs for identical deposition time become more reproducible. The reproducibility of the W thickness is acceptable during a second period, or "validity period," of the CVD reactor. The cumulative thickness of metal which can be deposited on test wafers with an acceptable reproducibility is about 4-5 µm. The H₂ reduction of WF₆ takes place on the surface of W layers grown via the Si reduction of WF₆ and starts after an induction or incubation time of 3 to 12 min (Fig. 3). Since this induction time varies erratically, the total thickness of W films produced for a given deposition time lies within a 75 or 50 nm wide range (Fig. 3), depending upon the H₂ partial pressure used. The induction time is observed to be shorter on Bdoped than on As-doped silicon wafers. Also, the induction time (measured in the center of the test wafers) is



Fig. 2. Position of Si wafers in the CVD reactor and different zones on wafers considered for W thickness measurements.

found to be independent of the position of the test wafers in the CVD reactor. The deposition rate of W films deduced from the slope of straight lines given in Fig. 3 is 8 and 5.5 nm/min at 700 and 350 mtorr of hydrogen, respectively. In other words, the deposition rate is proportional to the square root of the H₂ partial pressure. This result is in good agreement with the deposition rate dependence on H₂ partial pressure already reported in the literature (3, 6, 10). After deposition of a cumulative W thickness of about 4-5 µm on the test wafers, a W deposit formed and spread rapidly over the surface of the quartzware, especially over the part of the quartz boat in the vicinity of the test wafers. The adhesion of this W deposit was rather poor, and W flakes can appear in the quartz tube. The validity period is followed by a third period or "decline period" of the CVD reactor. As previously mentioned (6), during this decline period, the deposition rate of W films decreases significantly.

Thickness uniformity of tungsten films.—The mean W thickness was determined in zones 1 to 9 on the test wafers processed during the validity period of the CVD reactor. The mean deposition rate of W in each zone calculated from the W thickness and total deposition time (including induction time) is plotted as a function of wafer position in the quartz boat (Fig. 4). The deposition rate is found to be independent of the type of dopant implanted in the Si substrates. For each data point reported in Fig. 4 (a, top), the deposition rate corresponds to a mean value obtained for two successive deposition runs performed at an H₂ partial



Fig. 3. Tungsten thickness vs. deposition time at a H_2 partial pressure of: (a) 700 mtorr; (b) 350 mtorr. Stabilization period of the CVD reactor: diamond-shaped symbols. Validity period of the CVD reactor: W films deposited on boron doped (circular symbols) and arsenic doped (triangular symbols) silicon substrates.

pressure of 700 mtorr. The uniformity of the deposition rate within the wafers placed in rows D and E is excellent for the W deposition performed at the beginning of the validity period (curves in dashed line). For wafers positioned in row C (upstream side in the CVD reactor), the uniformity is good within the wafer except in zone 1, where the deposition rate is divided by a factor of 2. At the end of the validity period (curves in solid line), the deposition rate decreases progressively within the wafers from the upper zone to the lower zone. In addition, the deposition rate is lowered on wafers placed in row E (downstream side in the CVD reactor). The value of the deposition rate given in Fig. 4 (b, top) corresponds to a mean value calculated for five successive deposition runs carried out at the end of the validity period. The uniformity of the deposition rate of these films produced at an H₂ partial pressure of 350 mtorr is acceptable within wafers positioned in rows C and D except in upper zones 1 and 2. In addition, for wafers placed in row C, a slightly lower deposition rate is also observed in zone 4.

Selectivity of the tungsten deposition process.—The density of W nuclei grown on the surface of a PSG mask for the test wafers placed in rows C and D was investigated as a function of the thickness of W films. The curves in Fig. 5 exhibit an exponential relationship between the density of W nuclei and the thickness of W films. The development of W nuclei and the thickness of W films. The development of C nuclei on the surface of downstream wafers (position D) is observed to be faster than on upstream wafers (position C) regardless of the type of dopant implanted in the Si substrates. In addition, the nuclei density is independent of the partial pressure of hydrogen or of the deposition rate of W films. Under the experimental conditions investigated, W films up to 220 nm in thickness were produced with a perfect selectivity (less than one W nuclei within a surface area of 2500 μ m²).

The nuclei density was determined on thermally oxidized dummy wafers placed in rows C, D, E, and F along lane 4 in the opposite position to the test wafers. The number of W nuclei was measured on the oxide surface after five successive deposition runs carried out during the validity period of the CVD reactor. The cumulative thickness of W films deposited on the test wafers was about 900 nm. The density of W nuclei on the oxidized dummy wafers measured along the diameter of wafers parallel to the axis of the quartz tube was found to be dependent on the wafer position (Fig. 6). The maximum nuclei density on each dummy wafer slightly shifts towards the downstream side. Furthermore, this maximum number of W nuclei on the oxide mask increases considerably from position C to position F in the CVD reactor.

Discussion

The Si reduction of WF_6 or first deposition step was found to occur on test wafers regardless of the number of deposition runs already performed in the reactor. In other words, this first step of W deposition is independent of the history of the CVD reactor or of the cleanliness of the quartzware. Moreover, the thickness of these W films evaluated at about 15 nm from profilometer measurements is identical to that obtained on undoped Si substrates (6). An excessive silicon erosion which can occur on heavily doped Si substrates (2) or with traces of oxygen in WF_5 -H₂ mixtures (7) was not observed under our experimental conditions.

The onset of the H_2 reduction of WF_6 on W films produced during the first deposition step can be delayed from a few minutes to several hours depending upon the cleanliness of the CVD reactor. The induction time of 3-12 min occurring during the validity period of the reactor was not observed on undoped silicon wafers (6). The mechanism of this reduction reaction of WF_6 involves several elementary surface reactions such as the dissociative adsorption of molecular hydrogen and the reaction between the adsorbed hydrogen and fluorine atoms. The induction time reveals an inhibition of the surface reactions caused by the poisoning of the W surface by dopant atoms or native silicon oxide residue. This incubation period for the H_2 reduction is particularly long using a freshly cleaned



Fig. 4. Deposition rate of W films vs. wafer position at a H₂ partial pressure of: (a) 700 mtorr; (b) 350 mtorr. First part (dashed line) and second part (solid line) of the validity period of the CVD reactor. W films deposited on boron doped (open symbols) and arsenic doped (closed symbols) silicon substrates.

quartz reactor. During the stabilization period of the CVD reactor, water vapor is probably given off by the quartz surface and a native silicon oxide layer can grow on Si wafers. After flushing the WF_6 - H_2 mixture for several hours through the CVD reactor at deposition temperature (285°C), the outgassing process of water vapor can be elimi-



Fig. 5. Density of W nuclei vs. W thickness on test wafers placed in row C (open symbols) and in row D (closed symbols).

nated and the growth of an active oxide layer can be avoided. The induction or incubation time is erratic and difficult to control. For 30 min of deposition, a mean thickness of W films of about 200 nm can be obtained with a dispersion of ± 37 and ± 25 nm for deposition runs performed at 700 and 350 mtorr of hydrogen, respectively. In other words, the reproducibility of this selective W deposition process in terms of W thickness is only ± 18 or $\pm 12\%$, depending upon the H₂ partial pressure used. However, this poor reproducibility is probably not a crucial problem for technological applications of these W films as diffusion barriers between aluminum and silicon. The decline period of the CVD reactor corresponding to the presence of a quasi continuous W deposit on the quartzware has also



Fig. 6. Density of W nuclei vs. wafer diameter and wafer position on thermally oxidized dummy wafers after deposition of a W cumulative thickness of about 900 nm on test wafers placed in the opposite position to dummy wafers.

been mentioned in a previous paper (6). The significant decrease in deposition rate was attributed to the effect of HF on the surface reaction which can appear under WF_{f} partial pressures as low as those used for the selective W deposition process.

During the validity period of the CVD reactor, the thickness uniformity of W films across a wafer and from wafer to wafer can be excellent $(\pm 3\%)$ for test wafers placed in rows D and E. The reduction in W thickness observed in zone 1 of the test wafers placed in row C (upstream side in the CVD reactor) results probably from a longer induction time of the H₂ reduction reaction in this deposition area. To minimize this loss of uniformity, the W deposition must be performed under 700 mtorr of H₂ instead of 350 mtorr. The deterioration in thickness uniformity on the lower part of the test wafers at the end of the validity period of the CVD reactor can result from a decrease in deposition rate of W films caused by the effect of HF on the deposition process according to the deposition mechanism previously proposed (6).

Very few attempts at a quantitative evaluation of the selectivity have been published (11-13). The results obtained on the evaluation of the density of W nuclei on the oxide mask depend on the method used for observing and counting the nuclei present on a part of the surface. The detection limit (Fig. 5) corresponds to one nuclei of tungsten in a square of 50 μ m which is observed by optical microscopy at a magnification of 1000. Tungsten nuclei 0.5 μm in size can be observed easily. This detection limit was considered acceptable for a first approach to applications of the selective W deposition process in VLSI technology. Under these conditions, 220 nm thick W films were produced with a perfect selectivity. Beyond this W thickness, the density of W nuclei increases exponentially as the W thickness increases. An exponential relationship between the density of W nuclei and deposition time has recently been mentioned (11). Furthermore, this study of the nucleation rate of tungsten on different oxides shows that the best selectivity is achieved from the use of a PSG mask. However, these results were obtained by observing the surface using scanning electron microscopy and cannot be compared directly with those reported in Fig. 5. In a previous study (6), the maximum W thickness able to be produced with a perfect selectivity was only 110 nm. The improvement in selectivity comes from a reduction in the deposition surface area by a factor of 10 and the use of a PSG mask instead of a LTO (SiO₂) mask.

The results reported in Fig. 6 suggest that the attack of the oxide mask by HF vapor may be the major factor responsible for the loss of selectivity. The HF partial pressure increases progressively from the upstream to downstream side in the CVD reactor and, consequently, the nucleation rate of W nuclei increases in the same way. The HF vapor emitted from the W layer grown on dummy wafers can adversely affect both selectivity and deposition rate on the test wafers. To avoid this drawback, the dummy wafers can be changed once or twice during the validity period of the CVD reactor. With the wafers parallel to the gas stream, the residence time of HF vapor in the reactor is reduced to a minimum; this experimental configuration is very favorable to the preservation of the selectivity of the deposition process.

Conclusion

This study has demonstrated that 220 nm thick W films can be deposited with a perfect selectivity on 12 test wafers simultaneously. During the validity period of the CVD reactor, the reproducibility on the W thickness is difficult to control due to an erratic induction time occurring at the onset of the H₂ reduction of WF₆. However, the thickness uniformity of W films across a wafer and from wafer to wafer is as good as $\pm 3\%$, which is suitable for the use of W films as contact and diffusion barriers in VLSI technology. The cumulative W thickness which can be deposited during the validity period of the reactor is estimated to be about 4-5 µm. In other words, 20 successive deposition runs with 12 wafers per run can be performed between each two cleaning sequences of the CVD reactor.

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