Characterization of Tungsten Deposited by GeH₄ Reduction of WF₆, and Its Application as Contact Material to Si


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ABSTRACT

W deposition by GeH₄ reduction of WF₆ is a promising alternative for W deposition from H₂/WF₆ and SiH₄/WF₆. The structure and composition of W layers deposited from WF₆ and GeH₄ are determined mainly by the deposition temperature. At temperatures between 300 and 400°C, W layers with a 15 bcc W crystal structure are formed. These W layers contain a substantial amount of homogeneously distributed Ge, roughly between 10 and 15 atomic percent (a/o). At higher temperatures, films are formed which consist of a mixture of β-W and α-W. At temperatures greater than 500°C, the layers consist exclusively of α-W, and the Ge concentration is less than 1 a/o. The amount of β-W in the film correlates with the resistivity and the amount of incorporated Ge. The incorporated Ge may promote the formation of the β-W phase. Other process parameters, such as the total pressure and the GeH₄/WF₆ ratio, have a minor effect on the structure and composition of the films. The β-W deposited at ~375°C is well suited for use as contact material to active Si areas of ULSI circuits. The contact resistivity of the β-W layers to 2 × 2 μm² n+ Si and p+ Si contacts is as low as the contact resistivity of annealed Al/Si 1%/Si reference samples. The contact resistivity to the p’ diffusions was slightly higher than to the n’ diffusions. No leakage current was observed, indicating that no harmful attack of the active Si areas occurred during the deposition of β-W. High resolution SEM pictures confirmed the absence of any significant Si consumption, enroachment, or tunnels at the Si interface. The β-W layers are stable and transform to α-W only at temperatures greater than 600°C during 30-min anneals. After transformation to α-W, silicidation to WSi₂ occurs. The β-W is an effective diffusion barrier between Al and Si. During 30-min anneals at 500°C, a β-W film as thin as 60 nm prevented all Al/Si interdiffusion. A 120 nm thick β-W film prevented Al/Si interdiffusion to at least 540°C. Finally, a deposition sequence consisting of the GeH₄ reduction of WF₆ followed by SiH₄ or H₂ reduction of WF₆, combines the excellent interface properties of the GeH₄/WF₆ process with the higher growth rate and better selectivity of the H₂/WF₆ or SiH₄/WF₆ process.

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One main problem which must be tackled for the fabrication of ultralarge scale integrated (ULSI) circuits, is the filling of the submicron contact holes between the active Si areas and the first level aluminum metallization. The requirements on the deposition technique as well as the contact plug material are stringent, making it difficult to find an appropriate solution. As far as the deposition technique is concerned, the decreasing lateral size and the unchanged height of the contact-hole, make it difficult to fill the high-aspect-ratio contact holes properly by evaporation or sputtering. The chemical-vapor deposition (CVD) technique provides, because of its better step-coverage, the possibility of filling the contact holes without formation of voids. Another process requirement is that during the filling of the contact hole only a limited amount of Si is consumed, because excessive Si consumption can lead to junction leakage. The requirements on the contact plug material are even more numerous. First, the material must prevent the interdiffusion between the first level Al metallization layer and the active Si areas. Without an effective barrier, Al-Si interdiffusion would lead to Al “spiking” through the active Si area resulting in severe junction leakage. Another important requirement is that the contact plug can withstand the high current densities occurring in submicrometer contact holes. The material must have a high resistance against electromigration. A good adhesion to Si and a low stress level are also important. A final mechanical demand on the contact-plug material is that it must be stable, so that no undesirable phase transformations or reactions occur during subsequent IC fabrication steps.
As far as the electrical properties are concerned, a low resistivity, but more important, a low contact resistivity to the active Si areas, is essential to reduce the switching time delays.

Chemical vapor deposition of W is a widely investigated process for the filling of submicron contact holes. Not only the material properties of W are highly advantageous (high electromigration resistance, low resistivity) but W also can be deposited relatively easily by CVD.

Tungsten is generally deposited by CVD from tungsten hexafluoride (WF₆) and hydrogen. However, during this process severe etching of the Si occurs, especially at the Si–SiO₂ interface of patterned wafers (encroachment). The formation of empty tunnels (wormholes) in the Si is also observed when the H₂WF₆ process is used. Because of the encroachment and tunnels, an additional barrier layer between the Si and W is needed to protect the Si. A barrier layer is also necessary when W is deposited on silicided contacts such as TiSi₂ and CoSi₂. The barrier layer must prevent Si consumption and TiF₃ formation in the case of TiSi₂ and CoSi₂. Examples of materials which are used as barrier layers are TiN and TiW. TiN and TiW generally are deposited by blanket sputter-deposition processes. As a result one cannot make use of the selective nature of the subsequent H₂/WF₆ CVD process. Moreover, the poor step-coverage of the TiN and TiW sputter-deposition process limits its use for submicrometer applications. A final drawback of the H₂ reduction of WF₆ (H₂ process) is the relatively high deposition temperature. The SiH₄ reduction of WF₆ (SiH₃ process) attracted interest in recent years because this process proceeds at lower temperature and, moreover, does not attack the Si interface. The absence of a reaction with the Si, however, leads to poor adhesion. Furthermore, the contact resistivity of SiH₃/WF₆ deposited W to p⁺ Si is high. Because of the above-mentioned drawbacks of the H₂ and the SiH₃ processes, we developed an alternative process which uses GeH₄ for the reduction of WF₆. Initial measurements on the properties of W deposited by this GeH₄ process showed promising results. Here we give a more detailed study on the structural, mechanical, and electrical properties of W deposited by GeH₄ reduction of WF₆. This process is suited for the direct deposition of W on active Si areas, and the main improvements of the GeH₄ process over the SiH₃/WF₆ processes are: better interface properties compared to the SiH₃ process, and improved efficiency and accuracy compared to the H₂/WF₆ process as a result of the redundancy of an additional TiN barrier layer.

Experimental Procedure

Depositions were carried out in two comparable cold-wall single-wafer reactors equipped with load-lock systems. In the first reactor depositions were carried out on 100 mm patterned Si/SiO₂ wafers in the "selective mode", i.e., deposition on Si and not on SiO₂. In the second reactor "blanket" depositions, i.e., W deposition across the whole wafer surface, were performed. In low-pressure systems the temperature difference between chuck and wafer can be high. For this reason we calibrated the temperature difference for all deposition conditions (only excluding the WF₆ flow to prevent deposition) with a thermocouple cemented on the front of a wafer, and with a pyrometer. The temperatures in this paper are thus calibrated wafer temperatures and not chuck temperatures. The error in the wafer temperature is estimated to be ±10°C. Before deposition the wafers were dipped in dilute buffered HF, rinsed in deionized water, and dried by pulling the wafers slowly out of the vapor of boiling isopropyl alcohol. Before deposition the reactor was purged with H₂ with the wafer at deposition temperature. The GeH₄ flow was introduced in the reactor a few seconds before the WF₆ flow.

The reflectivity of the growing W film was monitored in situ by measuring the intensity of a HeNe laser beam reflected from the surface. In this way, we could monitor the start of the deposition, the surface roughening and, when the W was deposited selectively on a Si/SiO₂ grid, the film thickness and growth rate.

To investigate the thermal stability of the W layers we annealed the films in a furnace filled with argon.

Results and Discussion

Crystallographic structure and composition of W deposited from WF₆ and GeH₄ as a function of deposition parameters. The crystallographic structure of W deposited by GeH₄ reduction of WF₆ depends on the deposition temperature. Below 300°C deposition temperature, only amorphous W–Ge mixtures formed. At higher temperatures crystalline W formed. This is shown in Fig. 1, where x-ray diffraction patterns are plotted for W films deposited at three different temperatures. Figure 1a shows that at 357°C the film deposited consists completely of β-W. At higher deposition temperatures the α-W phase also formed, leading to films consisting of a mixture of α-W and β-W. This is shown in Fig. 1b for a film deposited at 470°C. The relative amount of β-W in the film keeps decreasing with increasing deposition temperature until at 510°C 100% α-W films are formed, as is shown in Fig. 1c.

In the literature, β-W is described as a meta-stable phase with the A15 bcc crystal structure, which can be stabilized by oxygen or fluorine. We looked for fluorine and oxygen by particle induced x-ray emission (PIXE) analysis, but found none.

Fig. 1. X-ray diffraction patterns for W films deposited at (a) 357°C, (b) 470°C, and (c) 510°C.
our samples did not show any fluorine above the 0.5 a/o detection limit. The small amount of oxygen we found, was attributed to oxygen contamination at the surface. However, we did find with electron probe microanalysis (EPMA) and Auger electron spectroscopy (AES) relatively large amounts of germanium in our W films. This Ge was incorporated homogeneously throughout the W layer (Fig. 9a).

The amount of Ge in the film decreased with increasing deposition temperature from more than 10 a/o at temperatures below 375°C to less than 1 a/o at temperatures above 500°C. This is shown in Fig. 2, where the amount of incorporated Ge as measured by EPMA is plotted as a function of the deposition temperature.

Since the ratio of the Ge atom radius and the W atom radius is 0.99, which is larger than the critical Hägg ratio of 0.59,12 it is more likely that the Ge is incorporated substitutionally in the W lattice rather than interstitially. Since the ratio of the Ge and W radius is even larger than 0.95, it is, according to Ref. 26, to be expected that, as in CrGe, Mo₃Ge, and Nb₃Ge, the Ge is incorporated in W as W₃Ge, which has the β-W crystal structure. The amount of β-W in Fig. 1 and the amount of Ge in Fig. 2 show a similar deposition temperature dependence and this indicates that the amount of β-W is correlated to the amount of Ge in the film.

Since the x-ray diffraction pattern in Fig. 1a shows, moreover, no Ge, W₃Ge, or WGe₂ peaks, we conclude that the β-W phase in our films is stabilized by Ge, which is at least partly incorporated as W₃Ge. The formation of a W₃Ge compound also is supported since the predicted enthalpy of formation is slightly negative for W₃Ge.12

The deposition temperature is the main process parameter in determining the amount of Ge and thus the structure of the deposited W layer. Other process parameters, such as the total pressure and the GeH₄/WF₆ partial pressure ratio, had no significant influence on the W structure and composition. Note that this is in strong contrast to the related SiH₄ reduction of WF₆, where the SiH₄/WF₆ ratio is an important parameter in determining the structure (α-W, β-W, or amorphous) and composition (Si incorporation) of the deposited W.

Because for ULSI applications low-temperature deposition processes generally are preferred over high-temperature processes, we concentrated the research described in the following sections, mainly on W layers deposited at low temperatures, typically between 350 and 400°C. As mentioned above, the W layers deposited at these temperatures have the β-W crystal structure and contain approximately 10 a/o Ge.

The morphology of GeH₄/WF₆ deposited tungsten and its interface to Si and SiO₂—The morphology of W deposited by the GeH₄ process depended on the deposition temperature and thus also on the phase deposited (Fig. 3). Figure 3a is a cross-sectional SEM picture of a 280-nm thick β-W film deposited at 372°C, while Fig. 3b is a 570-nm thick, mainly α-W film, deposited at 445°C. The β-W film consists of thin long columns with a width ca. 60 nm, which end in small sharp peaks. In the case of thicker β-W films only the length of the needle-like columns increased. The morphology of the α-W film in Fig. 3b is clearly different; the width of the columns is much larger than in the β-W film. By comparing the thickness of the films, as measured from the cross-section SEM pictures, with the weight of the deposited layers, we found the expected density (19.3 × 10³ kg/m³) for W layers, indicating that the layers are fully dense and not porous. Dense layers are important for the application of these films as a diffusion barrier between Al and Si.

The surface of the β-W as well as the α-W is smooth and mirror-like. Figure 4b shows the excellent reflectivity of β-W deposited by the GeH₄ process in contrast to the reflectivity of α-W deposited by the H₂ process in Fig. 4a. In this figure the intensity of a HeNe laser beam reflected from the growing W surface is plotted vs. the deposition time. The decrease in the reflectivity due to surface roughening is clearly stronger for the H₂ process in Fig. 4a than for the GeH₄ process in Fig. 4b. For submicron lithography the smoothness of films deposited by the GeH₄ process is an advantage over the rough layers obtained using the H₂ process.

For proper performance of ICs, the Si source and drain areas must not be damaged during the deposition of the W layers. A severe damage of the Si areas leads to current leaks through the junctions and to deterioration of the device performance. The attack of Si by WF₆, for instance,
Fig. 4. Reflectivity as a function of the deposition time for W deposited by (a) the H$_2$ process, and (b) the GeH$_4$ process.

is why the H$_2$ process cannot be used without an additional barrier layer. The GeH$_4$ process is suited for the deposition of β-W directly on active Si areas, as is shown in Fig. 5a. This figure is a cross-sectional SEM picture of a wet-etched patterned Si-SiO$_2$ wafer on which β-W is deposited selectively by the GeH$_4$ process. Figure 5a shows that the Si consumption is less than the 3-nm resolution of the picture. Moreover, no tunnel structures or encroachment at the Si-SiO$_2$-W triple interface are visible. For comparison, Fig. 5b is a SEM picture of W deposited under almost the same conditions using the H$_2$ process. By comparing Fig 5a and b, the interface integrity obtained with the GeH$_4$ process is better than in the case of the H$_2$ process. The absence of any significant Si consumption, tunnels, or encroachment shows that W can be deposited by the GeH$_4$ process directly on Si without damaging the active Si areas. This makes the GeH$_4$ process at temperatures below 400°C suited for contact applications to Si, especially in the case of shallow junctions.

At higher temperatures the reaction between WF$_6$ and Si is not inhibited completely by the GeH$_4$ process. The Si consumption, however, is still limited (<40 nm) compared to the Si consumption of the H$_2$ process (Fig. 5b).

In our opinion the integrity of the Si interface at temperatures below 400°C, is due to the protection of the interface by an adsorbed GeH$_4$ layer. As mentioned before, the GeH$_4$ flow is introduced into the reactor a few seconds before the WF$_6$ flow. From the literature GeH$_4$ decomposes very easily on Si surfaces at the temperatures and pressures used during the GeH$_4$ process. The WF$_6$ molecules therefore react with the adsorbed GeH$_4$ layer, leaving the Si intact. At high temperatures the Si consumption does occur, which is in agreement with thermodynamic calculations which showed that at temperatures above ca. 600 K the reaction between WF$_6$ and Si is thermodynamically more favorable than the reaction between WF$_6$ and GeH$_4$. The reason for the absence of tunnels may be that GeF$_2$ and H$_2$ are the main reaction products during the GeH$_4$ process; no HF is formed. HF, which is the main reaction product of the H$_2$ process, is necessary for the formation of tunnels.

A final benefit of GeH$_4$ which may contribute to the absence of any encroachment, is the ability of GeH$_4$ to remove the native oxide present on Si surface. A clean Si surface, free of native oxide, is essential for encroachment-free W films.

The adhesion of the β-W layers to Si was excellent. The layers never peeled off from the Si at any deposition pressure, temperature, or GeH$_4$/WF$_6$ ratio. This excellent adhesion to Si is obtained without any harmful reaction with the Si. For blanket depositions the W must nucleate on the SiO$_2$ wafer. This is achieved by increasing the GeH$_4$ and WF$_6$ partial pressures compared to the selective deposition conditions. An increase in the deposition temperature also promotes the nucleation on SiO$_2$. The adhesion of blanket β-W deposited on SiO$_2$ at low temperatures, is reasonable. The β-W layers do not peel off from the SiO$_2$ surface. The adhesion of α-W layers to SiO$_2$ is good. The α-W layers deposited at temperatures above 450°C generally pass the "Scotch tape test." An important reason why GeH$_4$/WF$_6$-deposited...
W layers do not peel from the substrate is that the layers can be deposited with a very low intrinsic stress.33

The excellent adhesion obtained with the GeH4 process is in strong contrast to the adhesion of W layers deposited by the SiH4 process. These layers peel off spontaneously from the Si substrate especially at low temperatures or high SiH4/WF6 ratios when Si is incorporated in the W layers.9

Electrical characterization.—Resistivity.—The resistivity of the β-W layers was approximately 200 μΩ cm. This is considerably higher than the 9 μΩ cm resistivity known for thin α-W films. With increasing deposition temperature and thus increasing α-W content, the resistivity of the films decreased from 200 μΩ cm for 100% β-W layers deposited at 350°C, to 10 μΩ cm for Ge-free α-W layers deposited above 500°C (Fig. 7).

For high-speed ICs a low resistivity is advantageous and thus the 200 μΩ cm of the β-W films seems at first sight rather high. However, for the application of β-W layers as contact material in submicrometer contact-holes, a relatively high resistivity is acceptable. This is because the contribution of the β-W resistance to the total resistance is small compared to the contribution of the contact resistance. For a submicrometer contact hole, with a diameter of 0.5 μm which is filled to a height of 500 nm with 200 μΩ cm β-W, the resistance of the W plug is 5 Ω. The contact resistance is ten times higher, namely 50 Ω for a typical contact resistivity to Si of 1 x 10^-7 Ω cm². This shows that for contact-hole filling a low contact resistivity to Si is far more important than a low specific resistance.

Diode leakage current.—To evaluate the leakage current properties, β-W was used as contact material in a washedge emitter bipolar process in which Al(1%Si) is applied normally as interconnect material.34 The Al(1%Si) washed-emitter bipolar process is characterized by extremely low-base leakage currents. The same extremely low-base leakage currents also were obtained using the β-W as contact material. This confirms that the active Si is not attacked by WF6 during the deposition of W by the GeH4 process and is in agreement with the SEM pictures of the W-Si and W-Si-SiO2 interface shown in Fig. 5a.

The better contact resistivity of W deposited by the GeH4 process compared to W deposited by the SiH4 process is due probably to the reduction of the native oxide by GeH4.32 We speculate that a longer exposure of the active Si areas to GeH4 before WF6 is introduced, may decrease the contact resistivity further.

Contact resistivity.—We measured the contact resistivity between β-W layers and As-doped n+ Si and B-doped p+ Si for several doping concentrations of the Si, with a Kelvin resistance structure. The results are presented in Table 1 and 2, together with the results of an Al(Si 1%)/Si reference sample which is annealed at 400°C. The doping concentration at the surface is estimated from SUPREM-3 simulations.34 The defined contact area was 2 x 2 μm². The contact resistivities were corrected for the enlargement of the contact openings during processing.

Table 1 shows that the contact resistivity of β-W to n+ Si and p+ Si is comparable to the contact resistivity of an annealed Al(1%Si)/Si sample. The contact resistivity of β-W to p+ Si is almost the same as to n+ Si. This is better than the contact resistivities obtained with the SiH4 process to p+ Si, which generally are 5 to 10 times higher than to n+ Si.14-16 After an additional annealing step at 500°C, the contact resistivity of the Al(1%Si) to Si increased due to Si precipitation. The contact resistivity of the β-W to Si did not increase and is more stable thermally.

When contact holes with dimensions below 1 μm are filled with sputtered Al(1%Si), the contact resistivity increases sharply due to Si precipitation. The reliability of the contact decreases due to the poor Al step-coverage. For submicron contact holes contacted with CVD β-W these problems should not occur, indicating the importance of the GeH4 process for the filling of submicron contact holes.

The better contact resistivity of W deposited by the GeH4 process compared to W deposited by the SiH4 process is due probably to the reduction of the native oxide by GeH4.32 We speculate that a longer exposure of the active Si areas to GeH4 before WF6 is introduced, may decrease the contact resistivity further.

Thermal stability.—Annealing of β-W films.—We investigated the thermal stability of the β-W layers by monitoring the change in resistivity, crystal structure, and composition after several annealing steps. The annealing time was 30 min and the annealing temperatures were varied between 500 and 700°C. The as-deposited samples consisted of 200-nm β-W with a resistivity of approximately

| Table 1a. The contact resistivity of β-W and Al(1%Si) for various doping concentrations. |
|----------------------------------|-----------------|-----------------|-----------------|
| Sheet resistance active Si areas (Ω/square) | Doping level at n+ Si surface (atom/cm²) | Contact resistivity β-W/n+ Si (Ω cm²) | Contact resistivity Al(1%Si)/n+ Si (Ω cm²) |
| 3 | 1 x 10^20 | 3.8 x 10^-7 | 7.5 x 10^-7 |
| 30 | 1.4 x 10^20 | 2 x 10^-8 | 2.5 x 10^-4 |
| 1800 | 2.3 x 10^20 | 1.2 x 10^-8 | 2.3 x 10^-4 |
| 2000 | 1.9 x 10^20 | 7.5 x 10^-7 | 5 x 10^-4 |
| 40 | 6.5 x 10^20 | 1.0 x 10^-8 | 4 x 10^-4 |
| 110 | 2.9 x 10^20 | 2.2 x 10^-8 | 1.1 x 10^-4 |

| Table 1b. The contact resistivity of β-W and Al(1%Si) to p+ Si for various doping concentrations. |
|----------------------------------|-----------------|-----------------|-----------------|
| Sheet resistance active Si areas (Ω/square) | Doping level at p+ Si surface (atom/cm²) | Contact resistivity β-W/p+ Si (Ω cm²) | Contact resistivity Al(1%Si)/p+ Si (Ω cm²) |
| 9 | 1.9 x 10^20 | 7.5 x 10^-7 | 5 x 10^-4 |
| 40 | 6.5 x 10^20 | 1.0 x 10^-8 | 4 x 10^-4 |
| 110 | 2.9 x 10^20 | 2.2 x 10^-8 | 1.1 x 10^-4 |

Fig. 6. Cross-sectional SEM pictures of a blanket α-W film deposited at 445°C with the GeH4 process on a patterned Si-SiO2 wafer.
150 μΩ cm and a Ge concentration of 10 a/o. The substrate material was undoped Si (100). Annealing the β-W films for 30 min at temperatures below 600°C had no effect on the resistivity of the film. After annealing at 600°C, the resistivity of the sample decreased with 10% to 135 μΩ cm. Annealing the sample for 30 min at 700°C resulted in a resistivity decrease of 30% to a resistivity of 100 μΩ cm. Annealing temperatures above 700°C cause the layers to peel off from the substrate. The x-ray diffraction pattern of the as-deposited β-W film, and the films annealed at 600 and 700°C are shown in Fig. 8. The x-ray diffraction pattern in Fig. 8b shows that the resistivity decrease after the 600°C anneal is due to the transformation of part of the β-W to α-W. We could not identify the very small peak at 2θ = 23.5°. After annealing at 700°C all β-W peaks have disappeared, as is shown in the x-ray diffraction pattern in Fig. 8c. In this sample β-W is transformed to α-W and part of the W has reacted with the Si substrate to WSi2. Due to the silicidation to WSi2, the volume of the film increases resulting in a compressive stress in the film. With continuing silicidation the force at the WSi2/Si interface increases linearly with the WSi2 thickness until the force is higher than the adhesion force and the layer peels off the substrate. This is what happens when the films are annealed above 700°C. The transformation from β-W to α-W, and the WSi2 formation also was analyzed by AES and Rutherford backscattering (RBS). These two techniques allow us to monitor the change in the Ge concentration and distribution. The AES depth profiles are shown in Fig. 9 and the RBS spectra in Fig. 10. The analyses presented in Fig. 9a and 10a are carried out on the same sample as used for Fig. 8a, Fig. 9b and 10b are the same sample as in Fig. 8b, and Fig. 9c and 10c as in 8c. Figure 9a and 10a show that in the as-deposited sample, the Ge concentration is distributed uniformly throughout the β-W layer. The AES and RBS spectra in Fig. 9b and 10b show a decrease in the β-W film thickness and the formation of a transition layer between the W and the Si substrate. According to the x-ray diffraction pattern in Fig. 8b, this layer already contains some α-W but no WSi2 formation has taken place yet. In the 30 min, 700°C sample, the W layer thickness has decreased further and the W-Si transition region is, according to the x-ray analysis, transformed to WSi2. The Ge concentration in the WSi2 layer is very low and the Ge accumulates at the Si-WSi2 interface, as is particularly clear from the RBS spectrum in Fig. 10c. The AES depth profiles in Fig. 9b and c also show that Si has diffused through the W layer toward the surface.
As in IC process lines subsequent IC production steps are transformation to α-W and WSi₂ takes place. for α-W films deposited by the GeH₄ process. well below 600°C no stability problems are to be expected Annealing of α-W/Si structures.—When annealing of WSi₂ is stable up to 30 min anneals at 600°C. At higher temperatures transformation of α-W and WSi₂ takes place. As in IC process lines subsequent IC production steps are well below 600°C, no stability problems are to be expected for α-W films deposited by the GeH₄ process.

Applications of the GeH₄ process

Thin α-W layers deposited at 375°C by the GeH₄ process are suited for use as contact material to active Si areas of ULSI circuits. These thin barrier layers can be deposited without any sign of interdiffusion. A 30-min 600°C annealed film shows up clearly as a rough Si surface. Table II shows that at 600°C a 60-nm thick α-W film is an effective diffusion barrier for Al/Si interdiffusion. A 120-nm thick α-W film is effective up to 540°C. The barrier properties of α-W films deposited by the GeH₄ process are at least as good as the barrier properties of α-W deposited by the H₂ process.

In summary, the α-W phase deposited by GeH₄ reduction of WₓSi₃ is stable up to 30 min anneals at 600°C. At higher temperatures transformation to α-W and WSi₂ takes place. As in IC process lines subsequent IC production steps are well below 600°C, no stability problems are to be expected for α-W films deposited by the GeH₄ process.

Annealing of Al/α-W/Si structures.—When the first-level Al metallization is deposited directly on top of active Si areas, problems arise because of Al-Si interdiffusion. This problem can be circumvented by saturating the Al during deposition with a few atomic percent Si. This saturation has as a drawback that the Si can precipitate at the Si-Al interface giving rise to high contact resistivities. A diffusion barrier which prevents the Al-Si interdiffusion is considered necessary for submicrometer applications. We investigated the diffusion barrier properties of W deposited using the GeH₄ process by annealing several Al/α-W/Si stacks at different temperatures. The annealing temperatures were 500, 520, and 540°C and the annealing time was 30 min. The thickness of the α-W diffusion barrier was 20, 90, 120, and 250 nm. The Al overlayer was layered with a thin Ti film which forms Al₃Ti during the subsequent annealing. The solid solubility of Si in Al₃Ti is up to 15 a/o and thus the capacity for silicon uptake of the overlayer is increased compared to a pure Al overlayer. After annealing the stacks, the Al₃Ti overlayer and the α-W film were removed chemically from the Si surface. A breakdown of the α-W diffusion barrier during annealing shows up clearly as a rough Si surface with large craters due to the diffusion of the Si through the barrier into the Al. The results are presented in Table II. In this table a plus sign means that the barrier prevented Al/Si interdiffusion, whereas a minus sign means a breakdown of the diffusion barrier visualized by a rough Si surface. Table II shows that at 500°C a 60-nm thick α-W film is an effective diffusion barrier for Al/Si interdiffusion. A 120-nm thick α-W film is effective up to 540°C. The barrier properties of α-W films deposited by the GeH₄ process are at least as good as the barrier properties of α-W deposited by the H₂ process.

Thin α-W layers deposited at 375°C by the GeH₄ process were analyzed by secondary ion mass spectroscopy (SIMS) to verify the results presented in Table II. Analysis was performed using a VG IX70S SIMS apparatus. The primary beam was 0.01 A/m², 6 keV O₂. Positive secondary ions were detected. The SIMS depth profile in Fig. 11a shows that 60-nm W prevented the interdiffusion of Al and Si during an anneal at 500°C. The small amount of W in the overlayer in Fig. 11a is attributed to the start of WAl₁₂ formation. The SIMS depth profile in Fig. 11b shows the interdiffusion of Si and Al due to the breakdown of the diffusion barrier during an anneal at 540°C.

**Table II. Results of the diffusion barrier tests for several temperatures and α-W thicknesses.**

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<tr>
<th>α-W thickness (nm)</th>
<th>500°C</th>
<th>520°C</th>
<th>540°C</th>
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<td>21</td>
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<td>253</td>
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A plus means barrier prevented interdiffusion and a minus means breakdown of the barrier.
process. Additional advantages of this process are the reduction of the resistance of the contact plug due to the low resistivity of α-W deposited by the SiH₄ and H₂ process, the higher growth rate in the case of the SiH₄ process, and finally the amount of expensive GeH₄ is reduced. An example of a W layer grown in a sequence of the GeH₄ and H₂ process is shown in Fig. 12. This figure is a cross-sectional SEM picture of a 360-nm thick α-W film grown with the H₂ process on top of 50 nm β-W grown with the GeH₄ process. The selectivity obtained in this way compared better to the selectivity of a pure GeH₄ process although we did not obtain perfect selectivity. However, the demands on perfect selectivity are a little less stringent, since the possibility of removing stray nuclei by chemical-mechanical polishing is feasible.

Al also can be used on top of the β-W film since β-W films as thin as 60 nm prevent all Al/Si interdiffusion during 30 min anneals at 500°C.

The GeH₄ process also is suited for blanket applications. Since the adhesion on SiO₂ is better at higher temperatures the blanket deposition of α-W is more appropriate than the blanket deposition of β-W. The combination of the GeH₄ process with the SiH₄ or H₂ process is also versatile for blanket-deposition processes.

Conclusion

This study clearly shows that the W-CVD process which uses WF₆ and GeH₄ as reactants, is suited for the deposition of W directly on active Si areas. With this process β-W films containing ~10 a/o Ge can be deposited selectively at ~575°C directly on active Si areas without any harmful Si consumption, tunnels or encroachment. Moreover, the contact resistivity to n⁺Si and p⁺Si is low, the adhesion to Si excellent, and the β-W stable up to 600°C.

On top of this selectively deposited β-W layer, W growth can be continued in the same reactor by either the H₂ or SiH₄ process in a selective or blanket mode. Also Al can be used on top of β-W since β-W is a good diffusion barrier to prevent Al/Si interdiffusion. Additional advantages of the GeH₄ process include; low deposition temperature, small grain size, and smooth layers.

In summary, the major advantage of the GeH₄ process over other W-contact fill processes is that W can be deposited directly on Si and no additional TiN or TiW diffusion/nucleation layers are required.

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Low Stress Oxide-Polysilicon Sandwiched Microbridges

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ABSTRACT

Residual stresses in thin films have an important bearing on the formation of free-standing microstructures using conventional silicon technology. Thermal processing constraints become even more restrictive when multilayer composite microstructures are required. We report here on the fabrication of silicon dioxide-polysilicon-silicon dioxide microbridges with low residual stresses on crystalline silicon substrates using appropriate annealing procedures and an anisotropic etch.

Microsensors for temperature, pressure, fluid flow, and other macroscopic variables have been actively investigated and reported in the literature. Almost all such applications require insulator films to provide thermal and/or electrical isolation and to enhance the mechanical integrity of the fabricated microstructures. Silicon nitride films have been used for these purposes, but then the process becomes incompatible with conventional bipolar IC fabrication. Conventional silicon dioxide yields much higher sensitivities compared to polycrystalline silicon. However, free-standing cantilevers/microbridges/membranes are difficult to achieve because of the residual stresses in these films from high temperature thermal processing and from mis-matches in physical properties with the substrate; this often results in highly deformed/cracked/broken structures.

In this paper we report on the fabrication of oxide-polysilicon-polysilicon dioxide microbridges with low residual stresses on crystalline silicon substrates using appropriate annealing procedures and an anisotropic etch.