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A STUDY ON THE THERMODYNAMICS AND KINETICS OF TUNGSTEN DEPOSITION
BY \( WF_6 \) AND \( GeH_4 \)

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Abstract. In this paper a thermodynamic and kinetic study of the new deposition process
of tungsten on silicon (100) from tungsten hexafluoride \( WF_6 \) and germane \( GeH_4 \) is
presented. Thermodynamic calculations as well as experiments show, that the reaction
occurring during deposition is:

\[
WF_6 + 3 GeH_4 \rightarrow W + 3 GeF_2 + 6 H_2
\]

The growth rate as a function of process parameters is obtained for selective depositions
in the temperature range from 600 to 800 K, and a total pressure range from 150 to 1000
mTorr. Experiments show that the germane reduction of tungsten hexafluoride is 0.9
order in \( WF_6 \), - 0.2 order in \( GeH_4 \) and zero order in \( H_2 \). The activation energy is 34
kJ/mol. These kinetic data of the \( GeH_4/WF_6 \) process differ markedly from the kinetics
of the recently much studied \( SiH_4/WF_6 \) process.

A fascinating observation is that the deposition rate does not change when \( SiH_4 \) is added
to the \( GeH_4/WF_6 \) mixture, while, on the contrary, a small amount of \( GeH_4 \) reduces the
growth rate from a \( SiH_4/WF_6 \) mixture considerably. The kinetic differences between the
at first sight similar \( GeH_4/WF_6 \) and \( SiH_4/WF_6 \) process are used to get a better insight in
both processes.

I Introduction

The need for high-density Integrated Circuits (IC's) has involved considerable research effort in
the metallisation of submicron IC's. One of the most investigated metallisation processes is the
deposition of tungsten by Chemical Vapor Deposition (CVD) \(^1\). This technique is very promising not
only, because the tungsten can be used as a low-resistivity shunt material for the gate, but the
tungsten is also a good diffusion barrier, which prevents the interdiffusion of Si source- and drain
areas with the aluminium metallisation \(^2\). In some cases W can also be used as an interconnect
material between two metallisation levels in a multilevel ULSI circuit. The CVD technique ensures
that submicron contact holes can be filled with an excellent stepcoverage and further provides the
possibility of selective deposition: i.e. deposition on Si and not on SiO\(_2\). This saves one lithographic
step and so increases the efficiency of the fabrication of an IC.

The most commonly used precursor molecule for W-CVD is tungsten hexafluoride \( WF_6 \).
Because the \( WF_6 \) molecule does not decompose spontaneously on a tungsten surface, a reductor is
needed to strip the fluorine atoms from \( WF_6 \). Several reductors have been investigated for this
purpose. First of all Si provided by the substrate is a very effective reductor for \( WF_6 \) \(^3\). But this

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reaction can only proceed until the selflimiting thickness has been reached, i.e. until the growing tungsten layer shuts off the interaction between the Si substrate and the WF$_6$. To continue deposition, H$_2$ can be used for the reduction of WF$_6$ (H$_2$ process) $^{7,8}$. The reduction of WF$_6$ by H$_2$ is a thoroughly investigated process, but still suffers from problems as, silicon consumption of the substrate, encroachment, wormholes, a low deposition rate ($<$ 200 nm/min), rough layers, and a relatively high deposition temperature (500 °C). To overcome these problems, SiH$_4$ is used, from 1987 on, as a reductor for WF$_6$ (SiH$_4$ process) $^9$. This process produces, at low temperatures and with a high deposition rate, smooth layers without encroachment or wormholes and limited Si consumption. But the SiH$_4$ process suffers from problems as high contact resistance to p$^+$ Si $^{10}$, Si incorporation in the tungsten layer $^{11}$, or the formation of tungsten silicides $^{12}$. Moreover the reproducibility of the SiH$_4$ process is very bad due to the strong sensitivity of the growth process on the SiH$_4$/WF$_6$ partial pressure ratio. Because small changes in process parameters as temperature, total pressure or flow rate can result in unknown changes of the SiH$_4$/WF$_6$ partial pressure ratio at the wafer surface, it is very difficult to investigate the kinetics of the SiH$_4$ process.

Recently we introduced GeH$_4$ as a reductor for WF$_6$ (GeH$_4$ process) $^{13}$. GeH$_4$ is chemically similar to SiH$_4$ but because Ge does not dissolve in α-W $^{14}$ and does not easily form tungsten germanides $^{15}$, we hoped for a process, which would result in α-W films over a larger process window than the SiH$_4$ process. It was found that the GeH$_4$ process yields at temperatures above $= 500$ °C pure α-W layers while below this temperature also β-W with the A15 bcc crystal structure is formed. At temperatures below ±400 °C pure β-W is formed which is stabilised by relative large amounts of germanium (up to $= 12$ at.% Ge). One of the most striking differences of this GeH$_4$ process compared to the SiH$_4$ process is however that the growth process is not very sensitive to the GeH$_4$/WF$_6$ partial pressure ratio. This makes the reproducibility of the GeH$_4$ process far better than the SiH$_4$ process and the investigation of the kinetics of the process easier.

This paper will concentrate on the thermodynamics and kinetics of the chemical vapour deposition of W from WF$_6$ and GeH$_4$. Where ever possible we will compare the results of the GeH$_4$ process with the results of the SiH$_4$ process in order to get a better understanding of both processes.

II Experimental

Selective depositions were performed in a cold-wall single wafer reactor, which is equipped with a load-lock system. In this reactor the wafers are pressed against a graphite chuck which is heated by lamps. The temperature was controlled by a thermocouple in the graphite chuck. The temperature difference between chuck and wafer was calibrated for all deposition conditions by a thermocouple pasted on the front side of a wafer and by a pyrometer. This ensured a stable and reproducible wafer temperature. For the selective depositions we used 100 mm p-type (100) Si wafers, covered with thermally grown oxide. After patterning, the total exposed fraction of bare Si was less than 10%. 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 Ar and H$_2$ with the wafer at deposition temperature. Effects of the displacement reaction (i.e. the reaction of WF$_6$ with Si) were minimized in two ways. Either we let the displacement reaction take place at low temperatures (ensuring a thin W layer) before the GeH$_4$/WF$_6$ deposition started or we introduced the GeH$_4$ flow in the reactor a few seconds before the WF$_6$ flow. The conversion factor for the reaction gases (mole of reacted gas divided by mole of input gas) was less than 10%. The quality of the process gases was electronic grade. The thickness of the W layers was examined by Scanning Electron Microscopy (SEM), and in situ, by measuring the interference signal of a HeNe laser beam reflected from a W-SiO$_2$ grating.
III Thermodynamics

The main stable reaction products which can be expected to form during deposition from GeH₄/WF₆ are W, GeF₂, GeF₄, HF and H₂. With these reaction products the overall reaction can be described with only two variables, x and y:

$$WF₆ + x GeH₄ \rightarrow W + y GeF₂ + (x-y) GeF₄ + (6+2y-4x) HF + (4x-y-3) H₂$$  

(1)

Thermodynamic calculations performed with a computer program based on the Solgasmix program developed by Eriksson showed that, in our temperature and pressure regime (600 - 800 K, 150 - 1000 mTorr), the process tends to form as much GeF₂ as possible. This means that for each deposited W atom (which releases six F atoms) three GeF₂ molecules will be formed. To form three GeF₂ molecule the process needs also three GeH₄ molecules. The H atoms released by the GeH₄ molecule, form H₂ molecules because from the original 6 F atoms there are no fluorine atoms left to form HF. So according to the thermodynamic calculations we can write for the overall reaction:

$$WF₆ + 3 GeH₄ \rightarrow W + 3 GeF₂ + 6 H₂$$  \[ΔG = -830 \text{ (kJ/mol)} \text{ at 700 K} \]  

(2)

This reaction equation gives, of all possible combinations of x and y in equation 1, the highest gain in Gibb's free energy. The gain in Gibb's energy for this reaction is, as a comparison, plotted together with the ΔG of the three most commonly used processes (Si, H₂ and SiH₄ reduction) as a function of temperature in Fig. 1. It can be seen in this figure that the gain in Gibb's free energy for the GeH₄ process is higher than the ΔG of the H₂ process and comparable to the ΔG of the Si reduction reaction. So, from a thermodynamic view, the unwanted initial severe Si substrate etching by WF₆, which is characteristic for the H₂ process, might be suppressed in the GeH₄ process.

![Figure 1. The change in Gibb's free energy as a function of temperature for four deposition processes.](image)

Reaction equation 2 is also checked experimentally by reacting a fixed closed volume of WF₆ and GeH₄. It was found by mass spectrometry and by measuring the amount of deposited tungsten that, only when the initial GeH₄/WF₆ ratio is equal or higher than three (i.e. the stochiometric ratio of equation 2), all WF₆ is converted to W. For GeH₄/WF₆ ratio's lower than three, part of the WF₆ remains unreacted because of depletion of GeH₄. The mass spectrometer showed also large amounts of H₂ and almost no HF. These experiments support strongly reaction 2 as the main reaction. The total pressure in the fixed volume should, at an initial ratio of GeH₄/WF₆ = 3, increase with a factor 9/4 according to reaction 2. We observe experimentally only an increase with a factor 6/4. This is because GeF₂ condenses on the cold reactor walls which is in accordance with literature.
IV Kinetics of the GeH₄ process

The WF₆ partial pressure has a strong influence on the deposition rate as is shown in Fig. 2. In this figure the deposition rate is plotted as a function of the WF₆ partial pressure for three different GeH₄ partial pressures. The temperature and total pressure are kept constant at 355 °C and 250 mTorr. The error in the deposition rate is for Fig. 2, but also for the following figures 2 to 7, estimated on 10 nm/min. When we average the slopes of the lines representing the dependence of the growth rate on WF₆ partial pressure for all three GeH₄ partial pressures we find that the averaged slope is 0.9 with a standard deviation of 0.1. This averaged line is drawn in Fig. 2. Since the results are plotted in Fig. 2 on a double logarithmic scale, the slope of this line represent the order of the reaction with respect to WF₆. So the reaction order is 0.9 in WF₆ with a standard deviation of 0.1.

A similar plot is made to determine the order of reaction with respect to GeH₄. The result is in Fig. 3 for three different values of the WF₆ partial pressure. Temperature and pressure are 355 °C and 250 mTorr. The drawn lines in Fig. 3 represent the averaged slope for the three WF₆ pressures. The reaction order is -0.2 in GeH₄ with a standard deviation of 0.1. The relative large standard deviation is due to the fact that we only varied the GeH₄ partial pressure over a small range.

Changing the carrier gas from H₂ to Ar did not influence the deposition rate as can be seen in Fig. 4. In this figure the carrier gas was changed from pure Ar via a 1:1 mixture of Ar and H₂ towards pure H₂.

The increase in growth rate with the total pressure is shown in Fig. 5 for two different wafer temperatures. The ratio of the partial pressures of WF₆, GeH₄, and H₂ remained constant at 1:1:50. Because the heat transfer from the chuck to the wafer depends strongly on the total pressure ¹⁷, we adjusted the chuck temperature for every deposition, in order to keep the same wafer temperature over the whole pressure range. We see in Fig. 5 that the order of reaction with respect to the total pressure is 0.7. This corresponds, within the experimental error, to the sum of the dependences on the partial pressures of the source gasses WF₆, GeH₄, and H₂.

The dependence of the deposition rate on temperature is presented in Fig. 6. The slope of the drawn lines is obtained by averaging the slopes of the Arrhenius plots at each of the three total pressures. The slope of the lines correspond to an activation energy of 34 kJ/mol with a standard deviation of 5 kJ/mol.

With this activation energy and reaction orders we calculated for all our deposition rates the pre-exponential factor A. This resulted in the following phenomenological rate equation:

\[ G = A \cdot [WF₆]^{0.9} \cdot [GeH₄]^{-0.2} \cdot e^{34000/RT} \]  

in this equation is:
- \( G \) growth rate in nm/min
- \( A \) \((9 \pm 2) \times 10^3\) in nm min⁻¹ mTorr⁻⁰·⁷
- \([WF₆]\) WF₆ partial pressure in mTorr. Exponent is 0·⁹ ± 0·₁
- \([GeH₄]\) GeH₄ partial pressure in mTorr. Exponent is -0·₂ ± 0·₁
- Activation energy \( E_a = (34 ± 5) \) kJ/mol
- Gas constant \( R = 8.314 \) J/mol.K
- \( T \) Temperature in K

This GeH₄ rate equation differs from the SiH₄ rate equation which is described in literature ¹⁸ as:

\[ G = \text{Constant} \cdot [SiH₄] \]  

(4)
Figure 2. Growth rate as a function of WF$_6$ partial pressure for three different GeH$_4$ partial pressures. The slope of the line is 0.9 ± 0.1.

Figure 3. Growth rate as a function of GeH$_4$ partial pressure for three different WF$_6$ partial pressures. The slope of the lines is -0.2 ± 0.1.

Figure 4. Growth rate as a function of H$_2$ and Ar partial pressure for two temperatures.

Figure 5. Growth rate as a function of total pressure for two temperatures. The slope of the lines is 0.7.
V Mixing of the reductors SiH$_4$ and GeH$_4$

In order to learn more about the GeH$_4$/WF$_6$ but also about the SiH$_4$/WF$_6$ deposition process we performed experiments in which we mixed the reductors GeH$_4$ and SiH$_4$. The results are in Fig. 7a and 7b. First we kept the GeH$_4$ and WF$_6$ flow constant and added some SiH$_4$ to the process. The result, which is in Fig. 7a, shows the W deposition rate as a function of the SiH$_4$ flow which was added to the GeH$_4$/WF$_6$/H$_2$ flow. It is clear from Fig. 7a that the influence of the SiH$_4$ flow is negligible. This is surprising since the SiH$_4$ process would give under these process conditions a higher deposition rate. This is shown in Fig. 7b. Here the W growth rate of the SiH$_4$ process is plotted as a function of the added GeH$_4$ flow. It can be seen in this figure that the growth rate drops significantly from 250 nm/min for a pure SiH$_4$ process to ± 60 nm/min when GeH$_4$ is added to the process.

These experiments show clearly that, in a mixture of SiH$_4$ and GeH$_4$, the kinetics of the GeH$_4$ deposition of W control the overall deposition process.
VI Discussion

The rate equation of the $\text{GeH}_4$ process (3) differs significantly from the rate equation of the $\text{SiH}_4$ process (4), which is linear in $\text{SiH}_4$ pressure and independent of the $\text{WF}_6$ pressure. The activation energy of the $\text{GeH}_4$ process shows a well defined value of 34 kJ/mol in contrast to the unclear low activation energy of the $\text{SiH}_4$ process. So, although the $\text{SiH}_4$ and the $\text{GeH}_4$ process look at first sight rather similar, the deposition processes are obviously controlled by different rate limiting steps.

The kinetics of the $\text{SiH}_4$ process is described in literature by Yu and Eldridge\textsuperscript{19} as a continuous sequence of two steps. One step is the decomposition of $\text{SiH}_4$ to $\text{Si}$. The second step is the deposition of $\text{W}$ by reducing $\text{WF}_6$ with this silicon. When we apply this model also to the $\text{GeH}_4$/$\text{WF}_6$ process we can compare the $\text{GeH}_4$ decomposition with the $\text{SiH}_4$ decomposition and the consecutive step i.e. the reaction of $\text{WF}_6$ with $\text{Ge}$ to form $\text{W}$ and $\text{GeF}_2$ can than be compared with the $\text{Si}$ reduction reaction of $\text{WF}_6$ to form $\text{W}$ and $\text{SiF}_4$.

Our experiment described in Section V with the $\text{SiH}_4$/$\text{GeH}_4$/$\text{WF}_6$ mixture showed that in this mixture the $\text{GeH}_4$ process controls completely the deposition process. This suggests strongly that the surface is covered with $\text{GeH}_x$ fragments and not with $\text{SiH}_x$. This implies that, under same conditions, the adsorption and decomposition is faster for $\text{GeH}_4$ than for $\text{SiH}_4$. This agrees with results from literature that $\text{Ge}$ layers can be grown from $\text{GeH}_4$ at considerable lower temperatures than $\text{Si}$ layers from $\text{SiH}_4$.

For the $\text{WF}_6$ reduction step the reaction rate of $\text{WF}_6$ with $\text{Si}$ to form $\text{SiF}_4$ is known to be very fast. At present no data is available about the reaction rate of $\text{WF}_6$ with $\text{Ge}$, but it is likely that this reaction is not as fast as the $\text{Si}$ reduction reaction.

So when we apply the concept of the continuous deposition sequence of the $\text{SiH}_4$ process also to the $\text{GeH}_4$ process then the clear differences in the kinetics of these two processes can probably be explained as follows. In the $\text{SiH}_4$ process the ratelimiting mechanism is the adsorption and/or decomposition of $\text{SiH}_4$ while the surface reaction of $\text{WF}_6$ with $\text{Si}$ is fast. In the $\text{GeH}_4$ process the adsorption and decomposition of $\text{GeH}_4$ is fast while the ratelimiting mechanism is the surface reaction between adsorbed $\text{Ge}$ and $\text{WF}_6$ to $\text{W}$ and $\text{GeF}_2$.

VII Conclusions

We conclude from thermodynamic calculations as well as from experiments that the deposition of $\text{W}$ from $\text{WF}_6$ and $\text{GeH}_4$ proceeds according to the following reaction equation:

$$\text{WF}_6 + 3 \text{GeH}_4 \rightarrow \text{W} + 3 \text{GeF}_2 + 6 \text{H}_2$$

$\Delta G = -830$ (kJ/mol) at 700 K

The formed $\text{GeF}_2$ deposits on the cold walls of the reactor.

The deposition rate is described by the following equation:

$$G(\text{nm/min}) = 9 \times 10^3 \left[ \text{WF}_6(\text{mTorr}) \right]^{0.9} \left[ \text{GeH}_4(\text{mTorr}) \right]^{-0.2} \exp\left(-\frac{34(\text{kJ/mol})}{RT}\right)$$

This rate equation differs clearly from the rate equation of the $\text{SiH}_4$ process and shows that these processes are controlled by different rate limiting steps. It is proposed that in the $\text{GeH}_4$/$\text{WF}_6$ process the surface reaction between adsorbed $\text{Ge}$ and $\text{WF}_6$ is rate limiting.
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