A STUDY ON THE THERMODYNAMICS AND KINETICS OF TUNGSTEN DEPOSITION BY WF₆ AND GeH₄

C.A. van Der Jeugd, G. Leusink, G. Janssen, S. Radelaar

► To cite this version:

C.A. van Der Jeugd, G. Leusink, G. Janssen, S. Radelaar. A STUDY ON THE THERMODYNAMICS AND KINETICS OF TUNGSTEN DEPOSITION BY WF₆ AND GeH₄. Journal de Physique IV Proceedings, 1991, 02 (C2), pp.C2-849-C2-856. 10.1051/jp4:19912101 . jpa-00249779

HAL Id: jpa-00249779

<https://hal.science/jpa-00249779>

Submitted on 1 Jan 1991

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

**A STUDY ON THE THERMODYNAMICS AND KINETICS OF TUNGSTEN DEPOSITION
BY WF_6 AND GeH_4**

C.A. VAN DER JEUGD, G.J. LEUSINK, G.C.A.M. JANSSEN and
S. RADELAAR

*DIMES, section Submicron Technology, Delft University of
Technology, P.O. Box 5046, 2600 GA Delft, The Netherlands*

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:

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 ^{3,4,5,6}. But this

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 ($< 200 \text{ nm/min}$), 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 $\alpha\text{-W}$ ¹⁴ and does not easily form tungsten germanides ¹⁵, we hoped for a process, which would result in $\alpha\text{-W}$ films over a larger process window than the SiH_4 process. It was found that the GeH_4 process yields at temperatures above $\approx 500^\circ\text{C}$ pure $\alpha\text{-W}$ layers while below this temperature also $\beta\text{-W}$ with the A15 bcc crystal structure is formed. At temperatures below $\pm 400^\circ\text{C}$ pure $\beta\text{-W}$ is formed which is stabilised by relative large amounts of germanium (up to $\approx 12 \text{ at.}\%$ 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 $100 \text{ mm p-type (100) Si}$ 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 GeH_4/WF_6 are W, GeF_2 , GeF_4 , HF and H_2 . With these reaction products the overall reaction can be described with only two variables, x and y:

Thermodynamic calculations performed with a computer program based on the Solgasmix program developed by Eriksson¹⁶ showed that, in our temperature and pressure regime (600 - 800 K, 150 - 1000 mTorr), the process tends to form as much GeF_2 as possible. This means that for each deposited W atom (which releases six F atoms) three GeF_2 molecules will be formed. To form three GeF_2 molecule the process needs also three GeH_4 molecules. The H atoms released by the GeH_4 molecule, form H_2 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:

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, H_2 and SiH_4 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 GeH_4 process is higher than the ΔG of the H_2 process and comparable to the ΔG of the Si reduction reaction. So, from a thermodynamic view, the unwanted initial severe Si substrate etching by WF_6 , which is characteristic for the H_2 process, might be suppressed in the GeH_4 process.

Figure 1. The change in Gibb's free energy as a function of temperature for four deposition processes.

Reaction equation 2 is also checked experimentally by reacting a fixed closed volume of WF_6 and GeH_4 . It was found by mass spectrometry and by measuring the amount of deposited tungsten that, only when the initial GeH_4/WF_6 ratio is equal or higher than three (i.e. the stoichiometric ratio of equation 2), all WF_6 is converted to W. For GeH_4/WF_6 ratio's lower than three, part of the WF_6 remains unreacted because of depletion of GeH_4 . The mass spectrometer showed also large amounts of H_2 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 $\text{GeH}_4/\text{WF}_6 = 3$, increase with a factor 9/4 according to reaction 2. We observe experimentally only an increase with a factor 6/4. This is because GeF_2 condenses on the cold reactor walls which is in accordance with literature¹⁷.

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 pressure¹⁷, 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:

$$G = A [\text{WF}_6]^{0.9} [\text{GeH}_4]^{-0.2} e^{-34000/RT} \quad (3)$$

in this equation is:

G	growth rate in nm/min
A	$(9 \pm 2) \times 10^3$ in nm min ⁻¹ mTorr ^{-0.7}
[WF ₆]	WF ₆ partial pressure in mTorr. Exponent is 0.9 ± 0.1
[GeH ₄]	GeH ₄ partial pressure in mTorr. Exponent is -0.2 ± 0.1
Activation energy	$E_a = (34 \pm 5)$ 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 literature¹⁸ as:

$$G = \text{Constant} [\text{SiH}_4] \quad (4)$$

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.

Figure 6. Growth rate as a function of temperature for three different total pressures.

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 $\text{GeH}_4/\text{WF}_6/\text{H}_2$ 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.

Figure 7. Growth rate for a mixture of the reductors GeH_4 and SiH_4 . a) SiH_4 added to the GeH_4 process and b) GeH_4 added to the SiH_4 process.

VI Discussion

The rate equation of the GeH₄ process (3) differs significantly from the rate equation of the SiH₄ process (4), which is linear in SiH₄ pressure and independent of the WF₆ pressure. The activation energy of the GeH₄ process shows a well defined value of 34 kJ/mol in contrast to the unclear low activation energy of the SiH₄ process. So, although the SiH₄ and the GeH₄ process look at first sight rather similar, the deposition processes are obviously controlled by different rate limiting steps.

The kinetics of the SiH₄ process is described in literature by Yu and Eldridge¹⁹ as a continuous sequence of two steps. One step is the decomposition of SiH₄ to Si. The second step is the deposition of W by reducing WF₆ with this silicon. When we apply this model also to the GeH₄/WF₆ process we can compare the GeH₄ decomposition with the SiH₄ decomposition and the consecutive step i.e. the reaction of WF₆ with Ge to form W and GeF₂ can then be compared with the Si reduction reaction of WF₆ to form W and SiF₄.

Our experiment described in Section V with the SiH₄/GeH₄/WF₆ mixture showed that in this mixture the GeH₄ process controls completely the deposition process. This suggests strongly that the surface is covered with GeH_x fragments and not with SiH_x. This implies that, under same conditions, the adsorption and decomposition is faster for GeH₄ than for SiH₄. This agrees with results from literature that Ge layers can be grown from GeH₄ at considerable lower temperatures than Si layers from SiH₄.

For the WF₆ reduction step the reaction rate of WF₆ with Si to form SiF₄ is known to be very fast. At present no data is available about the reaction rate of WF₆ with Ge, but it is likely that this reaction is not as fast as the Si reduction reaction.

So when we apply the concept of the continuous deposition sequence of the SiH₄ process also to the GeH₄ process then the clear differences in the kinetics of these two processes can probably be explained as follows. In the SiH₄ process the ratelimiting mechanism is the adsorption and/or decomposition of SiH₄ while the surface reaction of WF₆ with Si is fast. In the GeH₄ process the adsorption and decomposition of GeH₄ is fast while the ratelimiting mechanism is the surface reaction between adsorbed Ge and WF₆ to W and GeF₂.

VII Conclusions

We conclude from thermodynamic calculations as well as from experiments that the deposition of W from WF₆ and GeH₄ proceeds according to the following reaction equation:

The formed GeF₂ deposits on the cold walls of the reactor.

The deposition rate is described by the following equation:

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

This rate equation differs clearly from the rate equation of the SiH₄ process and shows that these processes are controlled by different rate limiting steps. It is proposed that in the GeH₄/WF₆ process the surface reaction between adsorbed Ge and WF₆ is rate limiting.

Acknowledgements

This work is part of the research program of the IOP - IC and the "Stichting voor Fundamenteel Onderzoek der Materie (FOM)", which is financially supported by the "Nederlandse Organisatie voor Wetenschappelijk Onderzoek (NWO)". We like to thank professor S. Wagner for pointing out reference 17 to us. We further thank T.G.M. Oosterlaken, Z.A. Ruchadze and J. Tóth for help in performing the experiments.

References

- [1] See for instance the proceedings of the « Workshops on Tungsten and Other Refractory Metals for VLSI Applications I to V », (Materials Research Society, Pittsburgh, PA)
- [2] BLEWER R.S., *Solid State Technol.* **29**, (1986) 117
- [3] BUSTA H.H. and TANG C.H., *J. Electrochem. Soc.* **133**, (1986) 1195
- [4] GREEN M.L., ALI Y.S., BOONE T., DAVIDSON B.A., FELDMAN L.C. and NAKAHARA S., *J. Electrochem. Soc.* **134**, (1987) 2285
- [5] KUIPER A.E.T., WILLEMSSEN M.F.C. and SCHMITZ J.E.J., *Appl. Surf. Sci.* **38**, (1989) 338
- [6] LEUSINK G.J., HEERKENS C.Th.H., JANSSEN G.C.A.M. and RADELAAR S., to be published in the proceeding of the « MRS 1990 Fall Meeting », (Materials Research Society, Pittsburgh, PA)
- [7] BROADBENT E.K. and RAMILLER C.L., *J. Electrochem. Soc.* **131**, (1984) 1427
- [8] MCCONICA C.M. and KRISHNAMANI K., *J. Electrochem. Soc.* **133**, (1986) 2542
- [9] KUSUMOTO Y., TAKAKUWA K., HASHINOKUCHI H., IKUTA T. and NAKAYAMA I., in Tungsten and Other Refractory Metals for VLSI Applications III, edited by V.A. WELLS (Materials Research Society, Pittsburgh, PA, 1988), p. 103.
- [10] HAMMAR M., ZHANG S.L., BUCHTA R. and JOHANSSON T., *Thin Solid Films*, **185**, (1990) 9
- [11] VAN DER JEUGD C.A., VERBRUGGEN A.H., LEUSINK G.J., JANSSEN G.C.A.M. and RADELAAR S., *Mater. Res. Soc. Symp. Proc.* **168**, (1990) 179
- [12] SCHMITZ J.E.J., BUITING M.J. and ELLWANGER R.C. in Tungsten and other Refractory Metals for VLSI Applications IV, edited by BLEWER R.S. and MCCONICA C.M., (Materials Research Society, Pittsburgh, PA, 1989), p. 27.
- [13] VAN DER JEUGD C.A., LEUSINK G.J., JANSSEN G.C.A.M. and RADELAAR S., *Appl. Phys. Lett.* **57**, (1990) 354
- [14] NOWOTNY H., BENESOVSKY F. and BRUKL C., *Monatshefte für Chemie* **92**, (1961) 365
- [15] POPOVA S.V. and FOMICHEVA L.N., *Inorg. Mater. (Engl. Transl.)*, **14**, (1978) 533
- [16] ERIKSSON G., *Chem. Scr.* **8**, (1975) 100
- [17] SLOBODIN D., ALJISHI S. and WAGNER S., *Mater. Res. Soc. Symp. Proc.* **98**, (1987) 291
- [18] SCHMITZ J.E.J., SUJCKER J.L.G. and BUITING M.J., in Tungsten and Other Refractory Metals for VLSI Applications IV, edited by BLEWER R.S. and MCCONICA C.M., (Materials Research Society, Pittsburgh, PA, 1989), p. 211.
- [19] YU M.L. and ELDRIDGE B.N., *J. Vac. Sci. Technol. A* **7**, (1989) 625