CHEMICAL VAPOR DEPOSITION OF TaSi₂ AND WSi₂ AT ATMOSPHERIC PRESSURE FROM IN SITU PREPARED METAL CHLORIDES

E. Blanquet, C. Vahlas, C. Bernard, R. Madar, J. Palleau, J. Torres

► To cite this version:

E. Blanquet, C. Vahlas, C. Bernard, R. Madar, J. Palleau, et al.. CHEMICAL VAPOR DEPOSITION OF TaSi₂ AND WSi₂ AT ATMOSPHERIC PRESSURE FROM IN SITU PREPARED METAL CHLORIDES. Journal de Physique Colloques, 1989, 50 (C5), pp.C5-557-C5-563. 10.1051/jphyscol:1989565 . jpa-00229597

HAL Id: jpa-00229597

<https://hal.science/jpa-00229597>

Submitted on 1 Jan 1989

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.

CHEMICAL VAPOR DEPOSITION OF TaSi_2 AND WSi_2 AT ATMOSPHERIC PRESSURE FROM IN SITU PREPARED METAL CHLORIDES

E. BLANQUET, C. VAHLAS, C. BERNARD, R. MADAR*, J. PALLEAU** and J. TORRES**

I.N.P.G., ENSEEG, L.T.P.C.M., BP. 75, F-38402 St Martin d'Hères, France

**I.N.P.G., ENSPG, L.M.G.P., BP.46, F-38402 St Martin d'Hères, France*

***C.N.E.T., CNS, chemin du Vieux Chêne, BP. 98, F-38243 Meylan, France*

RESUME - Les conditions expérimentales optimales de dépôt CVD de TaSi_2 et WSi_2 ont été définies à l'aide de calculs thermodynamiques préalables. Ces résultats ont été utilisés, en premier lieu, dans le cadre d'une étude expérimentale du dépôt chimique en phase vapeur à pression atmosphérique (APCVD) de siliciures de tantale à partir de chlorures métalliques créés in situ. Le procédé expérimental et les dépôts obtenus sont compatibles avec la technologie VLSI.

ABSTRACT - Optimum conditions for CVD of TaSi_2 and WSi_2 films were defined from thermodynamic calculations. These data were used as guidelines for the experimental investigation of the CVD of tantalum silicides at atmospheric pressure. The deposition process and the deposited films were found to be compatible with requirements for VLSI technology.

INTRODUCTION

Improvements in performance of integrated circuits and the trend towards VLSI technology require the replacement of polycrystalline silicon (poly-Si) by materials with a lower resistivity for use as gate electrodes and interconnects. Refractory metal silicides such as WSi_2 , TiSi_2 , TaSi_2 and MoSi_2 deposited by CVD appear as appropriate candidates for these applications /1,2/.

The present work deals with a combined thermodynamic and experimental investigation of the Atmospheric Pressure Chemical Vapor Deposition (APCVD) of TaSi_2 and WSi_2 thin films.

THERMODYNAMICS

The composition of both gaseous and condensed phases at equilibrium can be calculated by a computational method based on minimizing the total Gibbs energy of the chemical systems : Ta (or W)-Si-Cl-H-O-Ar /3/. To avoid technological difficulties linked to the transport of tantalum or tungsten chloride vapor and to improve the versatility of the set up, the metal precursor was prepared by in situ metal chlorination. Thermodynamic calculations for the Ta (or W)-Cl-O-Ar systems at equilibrium were carried out to determine the gas phase composition during metal chlorination /4/. Results on tungsten chlorination reported by /5/ were also taken into account. For these calculations the reactant species were Ta or W (in excess) in contact with chlorine diluted in argon; the variables were chlorination temperature and chlorine concentration. The results for tantalum and tungsten are presented in Figures 1a and 1b respectively.

Figure 1 : Calculated concentrations of metal chloride versus chlorination temperature; $\text{Cl}_2(\text{g})$: 0.1 moles, $\text{Ar}(\text{g})$: 0.9 moles. (a)- 10 moles of Ta; (b)- 10 moles of W.

In most of the temperature range investigated, chlorine is transformed essentially into the condensed chlorides Ta_2Cl_5 and WCl_2 . In the case of tantalum chlorination, the equilibrium gas phase is mainly composed of a mixture of tantalum tetrachloride, TaCl_4 , and pentachloride, TaCl_5 , in almost equal amounts; in the case of tungsten chlorination, it is principally composed of tungsten tetrachloride, WCl_4 , and dichloride. Condensed WCl_2 is totally evaporated over 1150 K. In both cases, the chloride partial pressures increase with temperature. No significant effect of gas phase dilution is observed.

It is worth noting that in order to achieve the same chloride partial pressures, tungsten chlorination temperature must be 100 degrees higher than that of tantalum.

As for metal chlorination, thermodynamic equilibrium calculations were also performed to simulate metal silicide CVD. Calculations provide the compositions and quantities of deposited phases and gaseous reaction products as a function of experimental parameters such as initial gas phase composition, total pressure and temperature. They are represented by means of "CVD phase diagrams" like those shown in figure 2 which point out the various tantalum or tungsten silicides phases deposited as a function of metal and silicon precursor partial pressures: an equimolar mixture of tantalum tetra- and pentachloride or tungsten tetrachloride and silane. These two CVD diagrams were constructed for a total pressure of one atmosphere and an argon partial pressure of 0.9 atm. Hydrogen partial pressure can thus be deduced in every point of the diagrams. Calculation temperatures are 950 K for tantalum and 1000 K for tungsten system.

Figure 2 : Calculated CVD phase diagrams deduced from the thermodynamic analysis; $P=1$ atm, $P_{Ar}=0.9$ atm. (a)- Ta-Si system, $T=950$ K; the experimental parameters investigated are located in the striped zone; (b)- W-Si system, $T=1000$ K.

EXPERIMENTAL PROCEDURE

Tantalum silicide films were deposited at atmospheric pressure in a vertical, cold wall, quartz reactor. This reactor is composed of a main tube which contains in its upper part the chlorination chamber. This is a thin coaxial tube, filled with 0.05 mm diameter refractory metal wire and heated by a resistance furnace. Chlorine passes through the chlorination chamber and the resulting gas phase meets the other gases in the lower part of the reactor (deposition chamber), above an inductively heated graphite susceptor. The reactive gas phase was composed of silane, hydrogen, argon, and tantalum chlorides ($TaCl_4$ and $TaCl_5$) produced by in situ tantalum chlorination. The chlorination temperature was 823 K; the chlorine flow rate was 2.13 cc/min while in order to obtain films of different composition, the silane flow rate was varied between 0.2 and 3 cc/min. Some low temperature deposited films were annealed at 1173 K for 110 min in an argon atmosphere. The deposited films were characterized by scanning electron microscopy and X-Ray diffraction technique. The resistivity of the deposited material was deduced from four-point probe measurements of the sheet resistance.

RESULTS

Figure 3 presents three typical X-Ray diffraction spectra of tantalum-rich ($TaSi_2 + Ta_5Si_3$), pure $TaSi_2$ and silicon-rich ($TaSi_2 + Si$) films-respectively a, b, c-deposited on mono-silicon or sapphire at $T = 950$ K and annealed. In the three spectra, hexagonal $TaSi_2$ with a preferential (001) orientation is identified. The presence of tetragonal Ta_5Si_3 and silicon are observed respectively for the tantalum- and silicon-rich films.

Figure 3 : X-Ray diffraction spectra of annealed tantalum silicide films.

(a)- $\text{Ta}_5\text{Si}_3 + \text{TaSi}_2$ film; (b)- TaSi_2 film; (c)- $\text{TaSi}_2 + \text{Si}$ film.

RBS measurements, performed on TaSi_2 films, are presented in Figure 4, before (spectrum a) and after (spectrum b) annealing. They show a decrease in the silicon concentration from the silicide-substrate interface to the surface where the Si/Ta ratio is 2.05. This variation may be due to the delayed arrival of the chlorides in the deposition zone. After annealing, films become more homogeneous. The average Si/Ta ratio is then reduced to 2.22, while still remaining at 2.05 at the surface.

The film thickness is 200 to 2000 nm corresponding for pure TaSi_2 deposition, to a growth rate varying from 30 nm/min at 950 K to 85 nm/min at 1150 K. At the lowest temperatures, the growth rate also increases with the Si/Ta ratio in the composition domain investigated.

The level of impurities was analysed by AES profiles and compared with the results obtained for pure TaSi_2 single crystals. The results, reported in figure 5 indicate no excessive carbon and oxygen contamination. It also seems that the deposited films do not contain chlorine, but the chlorine and tantalum Auger emission energies are too close to each other to confirm this with certitude.

The average grain size observed at the top surface falls from 1 μm for films deposited at $T = 1150$ K to less than 10 nm for those deposited at $T = 950$ K. The surface of the latter films is presented in the surface SEM photograph of figure 6a and it is mirror like, while the silicide-silicon substrate interface is plane (cross section SEM photograph of figure 6b). Surface and interface morphologies do not change with annealing.

The resistivity of the films deposited at $T = 950$ K is reported in figure 7 as a function of silane partial pressure and related film composition. For the as deposited metallic films it is about $200 \mu\Omega\cdot\text{cm}$. It increases drastically for the $\text{TaSi}_2 + \text{Si}$ layers while it decreases to about $60 \mu\Omega\cdot\text{cm}$ after annealing.

Films with a thickness greater than to 1.5–2 μm exhibited poor adhesion on substrates.

Figure 4 : RBS profile of TaSi_2 film. (a) As deposited; (b) After annealing.

Figure 5 : Auger electron spectra of TaSi_2 film.

Figure 6 : SEM micrographs of a tantalum disilicide film deposited at $T = 950$ K. (a) Surface; (b) Cross sectional view.

Figure 7 : Film resistivity versus silane partial pressure; $T = 950$ K; $\overline{P}_{Ar} = 8.98 \times 10^{-1}$ atm; $\overline{P}_{Cl_2} = 2.13 \times 10^{-3}$ atm. (a) As deposited; (b) After annealing.

DISCUSSION

The stripped area of the CVD phase diagram presented in figure 2a corresponds to the experimentally investigated section in the as given conditions. Although there is qualitative agreement between the thermodynamic predictions and the experiments, a slight misfit was observed as to the nature of the deposited phases obtained with different tantalum chlorides and silane partial pressures. This may be due to the quality of some thermodynamic data like those of the silicon chlorides, /6/, or to kinetic effects which are not taken into account in calculations. Nevertheless, in the authors opinion, this misfit is mainly due to the chlorination mechanism itself: it is presumed that instead of a direct reaction of the chlorine with the pure metal leading to the gaseous chlorides, the tantalum is continuously transformed into condensed subchlorides - mainly Ta_2Cl_5 - which cover its surface. These condensed subchlorides, by reacting with chlorine and gaseous products, are finally transformed into gaseous chlorides. Mass spectroscopy studies would be useful for a better understanding of this mechanism.

The characteristics of the films are quite similar to those previously reported (/2/ and references therein). The plane film-substrate interface suggests no silicide-silicon interdiffusion. Neither interface nor mirror like surface morphologies are influenced by annealing and, from this view point, the process is well suited to VLSI technology.

The disilicide films deposited on monocrystalline silicon or sapphire present, before and after annealing, a strong preferential orientation as shown by X-Ray diffraction spectra (figure 3), whereas similar films on predeposited polysilicon have no preferential orientation. This phenomenon indicates that the $TaSi_2$ growth is influenced by the crystalline structure of the substrate. The as deposited polycrystalline films have to be annealed to reach a resistivity of $68\mu\Omega.cm$ which is approximately 1.5 times higher than that of $TaSi_2$ monocrystal (30 to $50\mu\Omega.cm$ following different crystallographic directions /7/).

CONCLUSION

Tantalum disilicide films were prepared by CVD at atmospheric pressure from metal chlorides and silane. The characteristics of these films appear to be suitable for microelectronic applications and compatible with VLSI technology.

The in situ metal chlorination to produce the metal precursor can be correctly controlled and is a reliable technique in terms of reproducibility of results.

Calculations based on thermodynamic analysis of the gas system have been found useful in predicting the appropriate conditions for deposition there by avoiding tedious and lengthy series of CVD experiments.

REFERENCES

- /1/ Murarka, S.P., in "Silicides for V.L.S.I. Applications", (Academic Press, New-York, 1983).
- /2/ Bernard, C., Madar, R., Pauleau, Y., Solid State Technol., 32 (2), (1989).
- /3/ Vahlas, C., Baret, G., Million-Brodaz, J.F., Bernard, C., Madar, R., in "Proceedings of the 6th conference on CVD", edited by Porat, R., Jerusalem, Israël (1987) p.255.
- /4/ Blanquet, E., Vahlas, C., Madar, R., Palleau, J., Torres, J., Bernard, C., Thin Solid Films, submitted (1988).
- /5/ Teyssandier, F., Thesis, Grenoble, France (1981).
- /6/ Bernard, C., Vahlas, C., Million-Brodaz, J.F., Madar, R., in "Proceedings of the 10th International Conference on Chemical Vapor Deposition", edited by Cullen, G.W., Vol.87-8, (Electrochemical Society, Pennington, NJ, 1987), p.700.
- /7/ Thomas, O., Thesis, Grenoble, France (1986).