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CHEMICAL VAPOR DEPOSITION OF REFRACTORY METALS DISILICIDES: A REVIEW

R. MADAR and C. BERNARD

INPG, ENSPG, CNRS URA-1109, Domaine Universitaire, BP. 46, F-38402 St Martin d'Hères, France
"INPG, ENSEEG, CNRS URA-29, Domaine Universitaire, BP. 75, F-38402 St Martin d'Hères, France

RESUME

Les siliciures métalliques jouent un rôle de plus en plus important en technologie circuits intégrés silicium de type VLSI. Parmi les différentes techniques susceptibles d'être utilisées pour obtenir de manière reproductible, des couches minces de ces matériaux de bonne qualité, le dépôt chimique en phase vapeur (CVD) apparaît actuellement comme la plus performante. Le but de cette publication est de passer en revue les différents procédés, matériaux et résultats obtenus jusqu'à présent par cette méthode de dépôt en technologie VLSI. De plus, les procédés récents susceptibles de répondre aux exigences de la future technologie ULSI seront examinées.

ABSTRACT

The importance of metal silicides films in current VLSI technology is obvious. Among the different techniques which can be used to obtain high quality layers of these materials in a reproducible manner, the CVD emerges as the more promising solution. The purpose of this paper is to review the various chemical vapor deposition processes, materials and results reported so far for refractory metals disilicides in today's VLSI technology. In addition, potentially new CVD processes that could meet the future needs of the ULSI technology will be explored.

INTRODUCTION

The applications for metal silicides in the field of VLSI technology have increased dramatically in the recent years. Among the different phases which have been studied, refractory metal
disilicides such as WSi$_2$, TaSi$_2$, MoSi$_2$ and TiSi$_2$ have been selected for use as gates and interconnexions due to their relatively low resistivity and high thermal stability (1-6). These silicides are compatible with most IC wafer processing, offering good dry etch, adhesion, oxidation and contact properties (7-10). Substituting polycrystalline silicon by low resistivity refractory metal disilicides in gate metallization can overcome limitations in size reduction which stem for the high resistance of fine-line, doped poly-Si. At present, the disilicides films are deposited on poly-Si to shunt the poly-Si gate electrode. To simplify metallization schemes, this multilayer structure can be replaced by pure silicide film (11).

Several physical techniques have been used to form thin films of these silicides: evaporation of the metal followed by annealing, coevaporation of the metal and silicon, sputtering from the stoichiometric compound, cosputtering of metal and silicon. However, by using these techniques, several problems have been encountered (8-10) such as poor step coverage and irradiation damage caused by electron beams or sputtering. By comparison, Chemical Vapor Deposition with its advantage of high purity materials, good conformal coverage, uniform film thickness, possibility of selective deposition, high throughput and low cost processing is very attractive for the deposition of these materials.

The intent of this paper is to give a general overview of the work already done in the field of refractory metals disilicides CVD with indications of the present status of current research programs, especially in the field of selective deposition.

Two aspects of the CVD of metal silicides have been deliberately ignored in this review:

- The formation by CVD at high temperature of thick silicides films for protective coatings against corrosion since the range of temperatures generally used does not correspond to what can be tolerated in IC technology.

- The OMCVD of MSi$_2$ phases by pyrolysis of volatile molecular silicon-metal compounds (12-13) since most of these organic compounds are not available commercially, limiting for the moment the utilization of this promising technique.

Among the different works which have been reported for the CVD of these materials, the originality of our approach lies in the systematic use of thermodynamic equilibrium calculations before any experiment to predict the general trends of our process. Some of these calculations published in an elsewhere (14,15) are also recalled in this paper together with the experimental results recently obtained.
Several different CVD methods are used to deposit metal silicides films. These methods cover a wide range of processing temperatures and pressures, energy sources to obtain the chemical reactions involved and reactor designs.

For the definition of a CVD process for metal silicides, two parameters have to be fixed:

- The choice of the gaseous metal compound and silicon-bearing molecules which induces the chemical reactions involved in the process.
- The choice of the chemical vapor deposition system among the three basic types: atmospheric pressure (APCVD) low or very low pressure (LPCVD or VLPCVD) and enhanced LPCVD methods (Plasma PECVD or Laser LICVD).

As concern the first parameter, we will consider only the deposition of refractory metal disilicides films based on the reaction of a silicon bearing gas commercially available (e.g., silane, chlorosilanes) with a gaseous metal compound. For proper compositional control of a CVD film, the thermal stability (or the stability with respect to hydrogen) of the gaseous metal compound and the silicon-bearing molecules should be similar (16). According to this crude selection criterion, the most attractive metal precursors are the metal halides MoCl₅, MoF₆, TaCl₅, TiCl₄, WCl₆ and WF₆.

For practical purposes, only those which are easy to vaporize, handle and supply can be considered for IC manufacturing. Thus, among these metal halides we must consider first TiCl₄ and WF₆ which are liquid compounds with vapor pressures at room temperature sufficient to flow directly into a low pressure CVD reactor. Their flow rates can be easily monitored using mass flow controllers and they can be supplied with high purity at a reasonable cost. As a result, CVD reactors and deposition processes for titanium silicide (17, 18) and tungsten silicide films (7, 19, 20) are now commercially available.

Various investigations have demonstrated the feasibility of TaSi₂ (21, 23) and MoSi₂ (22, 24) CVD using TaCl₅ and MoCl₅ solid sources as the respective metal precursors. However, these reactive pentachlorides pose problems of corrosion, contamination and reproducibility which have impeded so far their implementation in device manufacturing. One possible solution that we have studied recently is the production of the gaseous chlorides in situ by passing chlorine through a pure metal bed (25). The results obtained by this method in the case of the APCVD of TaSi₂ (25) show that at least in this case, the in situ chlorination process can be well controlled and may produce reproducible amounts of tantalum chlorides TaCl₄, TaCl₅. A similar work is in progress for the CVD of WSi₂.
As concern the second parameter, the choice of the chemical vapor deposition technique, it depends on the nature of the silicide which has to be deposited.

For example, high quality films of TiSi2 have been obtained by APCVD, LPCVD and also PECVD while in the case of WSi2, starting from WF6 and SiH4, a LPCVD technique is needed in order to avoid gas phase nucleation problems.

PECVD systems have been used successfully for the production of high quality, smooth and reproducible MSi2 films but the as-deposited layers are amorphous and an annealing step is needed to obtain the required transport properties. Moreover, PECVD system cannot be used for a selective process.

Thus, it appears difficult to define at first the best system for the CVD of these materials. However, the actual trends are directed to the use of LPCVD, cold walls, single wafer, systems to avoid depletion effect during the deposition process.

THERMODYNAMIC EQUILIBRIUM CALCULATIONS

As the first step of CVD experimentation, equilibrium calculations based on a thermodynamic analysis of gas systems can provide an invaluable aid, guiding the selection of suitable gas mixture, temperature and other experimental conditions for the deposition of a given material.

There are two common approaches that can be used for equilibrium calculations. The first one is to consider only some chemical reactions and calculate the concentration of the different species at equilibrium. Most of the thermodynamic calculations performed in the case of the CVD of refractory metals disilicides are limited to this approach. Some of the reactions which have been used are the following.

\[
\begin{align*}
\text{TiCl}_4 + 3\text{SiH}_4 & \rightarrow \text{TiSi}_2 + \text{SiCl}_3 + 3\text{HCl} + 3\text{H}_2 \quad (26) \\
\text{MoF}_6 + 2\text{SiH}_4 & \rightarrow \text{MoSi}_2 + 6\text{HF} + \text{H}_2 \quad (27) \\
\text{TaCl}_5 + 2\text{SiH}_4 & \rightarrow \text{TaSi}_2 + 5\text{HCl} + 1.5\text{H}_2 \quad (28) \\
\text{TaCl}_5 + 2\text{SiH}_2\text{Cl}_2 + 2.5\text{H}_2 & \rightarrow \text{TaSi}_2 + 9\text{HCl} \quad (28) \\
\text{WF}_6 + 2\text{SiH}_4 & \rightarrow \text{WSi}_2 + 6\text{HF} + \text{H}_2 \quad (29)
\end{align*}
\]
The validity of this kind of calculation depends of the choice of the chemical reactions considered.

The second method which is generally preferred is a minimization of the Gibbs energy of the whole system, using the technique already described by many authors and previously performed successfully in numerous systems (30-32). With this method, all the conceivable species which can appear during the chemical reactions involved are taken into account. For a given set of reactants, total pressure and reaction temperature, the composition of both gaseous and condensed phases at equilibrium can be calculated.

Errors may arise from the use of incorrect thermochemical data or the omission of important species. So the first step in this method is to list the chemical compounds or species which are likely to be formed and be present in the system at equilibrium. Then, a judicious selection of the data reported in the literature and an estimation of unknown data must be done.

The thermodynamic data of the gaseous species which have been used in our calculations come from the "Scientific Group Thermodata Europe" (SGTE) and classical references sources (33, 36). For the condensed phases of metal-silicon systems, the selection of the most suitable thermodynamic data was based on the consistency of calculated and experimental phase diagrams. More often, this thermodynamic procedure shows that the scarce data available for the different solid phases of the M-Si (M = W, Mo, Ta, Ti) systems are not self consistent. A critical assessment of the phase diagrams leads to a new set of thermodynamic data required to start the equilibrium calculations (14, 15). Selected thermodynamic data used for these calculations are given in Table 1.

<table>
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<th>Comp.</th>
<th>( \Delta H^0_T )</th>
<th>( S^0_T )</th>
<th>( J/\text{atgr} )</th>
<th>( J/\text{Deg/atgr} )</th>
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<td>WSi₂</td>
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Table 1: Selected thermodynamic data for the four silicides of interest in IC technology
The thermodynamic equilibrium calculations performed in the different systems investigated were used to represent the equilibrium conditions during the deposition process in the form of "CVD phase diagrams". This kind of diagram shows computed phase boundaries for the condensed phases deposited at equilibrium as function of the experimental CVD parameters chosen. These boundaries separate ranges of input conditions under which specific condensed phases are computed to be equilibrium products. Example of these diagrams are given for different metal-silicon system in figure 1 together with the conditions chosen for these calculations.

Similar results have been obtained for some of these systems by other groups (28, 23) using different programs based also on the technique of minimization of the Gibbs free energy of the systems.

As examples of the information which may be obtained from these calculations, let us consider the results for metal chloride-silane-hydrogen systems with similar input conditions as shown in figure 1 for W, Ta and Ti. The three CVD phase diagrams present numerous domains and the principal evidence which comes out at first sight is the various extents of pure disilicide deposition domains. The TiSi2 case is quite promising for CVD experiments, while the WSi2 and TaSi2 ones are much more restricted.

An extensive investigation of the thermodynamic equilibrium calculations in these systems have been reported in an elsewhere (15). We will recall the main conclusions:

- Among the four disilicides WSi2, MeSi2, TaSi2, TiSi2, the latter seems to be the most suitable for a CVD process.
- The metal chlorides are thermodynamically more appropriate than the corresponding fluorides as metal sources.
- Replacing silane by dichlorosilane extends in all cases the pure MoSi2 deposition domain.

RESULTS

We will describe successively the reported results obtained so far for the four silicides of interest in IC technology.

Titanium disilicide : TiSi2

The reported work on the CVD of blanket TiSi2 include APCVD (37, 38) LPCVD (37, 39, 43) PECVD (37, 44) and LICVD (45, 47).
Fig. 1: Computed equilibrium "CVD phase diagrams" in the systems M-Si-H-Cl-Ar (M = Ta (a), Ti (b), W (c)) for the following experimental parameters: total pressure 1 atm, deposition temperature 720°C, argon partial pressure: 0.9
A general overview comes from the original work of Kemper et al (37) who have investigated the synthesis of TiSi$_2$ by APCVD, LPCVD and PECVD. The APCVD of TiSi$_2$ (37) performed in a temperature range of 800-1000°C and TiCl$_4$/SiH$_2$Cl$_2$ ratios of 1.5 to 4 resulted in rough films with poor adhesion which was attributed to gas phase nucleation during the deposition process. To improve these results, they investigated the LPCVD of this compound in a temperature range of 600-800°C, a pressure range of 0.1-5 torr and a TiCl$_4$/SiH$_4$ or TiCl$_4$/Si H$_2$Cl$_2$ ratios of 0.1 - 10.

During these experiments, they were the first to point out the selective character of this process and concluded that the deposition of TiSi$_2$ is inhibited by the presence of a native oxide layer. So in order to obtain a TiSi$_2$ film, it is necessary to deposit first a polysilicon layer by SiH$_4$ pyrolysis leading to a polycide structure. There is presently a general agreement on this procedure which has been used by almost all groups working on this subject.

They also indicated that the surface roughness of their films was unacceptable and suggested that it must be possible to obtain better results by an improvement of the vacuum system.

Effectively, soon after, better results were obtained by Reif et al (26, 41, 43) using a LPCVD cold wall reactor by a careful optimization of the deposition conditions. Smooth, reproducible low resistivity titanium disilicide films were obtained at a pressure of 67 mtorr, a temperature of 730°C and a SiH$_4$/TiCl$_4$ gas flow rate ratio of 20/2. They also demonstrated that the structure of the deposited films was extremely sensitive to the reactive gases flow rate ratios.

LPCVD of TiSi$_2$ has also been reported by Bouteville et al (39), using direct reaction of TiCl$_4$ with the silicon substrate in the presence of hydrogen in the temperature range 700-1000°C and a total pressure of 0.75 torr.

However, the influence of the total pressure parameter is still unclear, since we have obtained results as good as those just mentioned by APCVD in a cold wall reactor working in a temperature range of 600-900°C and a TiCl$_4$/SiH$_4$ ratio of 0.5 to 1 (38). This experimental work was based on the results of thermodynamic equilibrium calculations in the Ti - Cl - Si - H - Ar system as mentioned previously. High quality polycrystalline films with good surface smoothness were obtained by sequential deposition of amorphous silicon and titanium disilicide at a low growth rate (2 μm/h) which was achieved by decreasing both the deposition temperature (~ 600°C) and the partial pressures of the reactive gases. The resistivity of the as deposited films is in the range 15-25 μΩ x cm even for this low deposition temperature. Thus no supplementary annealing step was needed.
Another approach for the synthesis of TiSi$_2$ films is the use of the PECVD technique. The first experiment was made also by Kemper et al (37) in a parallel plate experimental reactor at a frequency of 300 kHz. The deposition occurs in a temperature range of 300-350°C and TiCl$_4$/SiH$_4$ gas flow rate ratio of 1 to 2. The as deposited films were reported to be smooth but amorphous and highly resistive. An annealing step at 750°C for one hour was needed to reduce the resistivity to 20 μΩ x cm.

Following these first attempts, a PECVD technique was also used by Rosler et al (44) to deposit TiSi$_2$ films at a temperature of 450°C, a frequency of 50 kHz and SiH$_4$/TiCl$_4$ ratio between 2.75 and 5.00. An annealing step at 600-650°C was also required to crystallize the as deposited amorphous films and to lower the resistivity to its usual value 15-20 μΩ x cm. A complete characterization of TiSi$_2$ films obtained by this technique has been made by Morgan et al (48).

This process has been improved recently by Hara et al (49, 50) using a horizontal type hot-wall plasma CVD reactor at 450°C, a pressure of 1.95 torr and an rf frequency of 50 kHz. By varying the TiCl$_4$/SiH$_4$ gas flow rate ratio from 0.23 to 0.09, they were able to change the composition of the films from 1.1 to 2.0. They have also demonstrated the importance of the annealing process for the stability of the TiSi$_2$/Si interface.

To complete this review of the work done in the field of the CVD of TiSi$_2$/Si polycide structure, we must briefly mention the results of the two LICVD investigations reported so far even if they are not especially good.

Gupta et al (45, 46) used an excimer laser to initiate a gas phase reaction process through the absorption of the laser energy by the TiCl$_4$ molecule, leading to the deposition of titanium silicide films at a substrate temperature above 350°C. The mostly amorphous as deposited films required to be annealed at a temperature of 650-700°C to reduce their resistivity.

A somewhat different LICVD pyrolicic process was reported by West et al (47) using a CO$_2$ laser. The deposition was carried out at a pressure of around 6 torr with a TiCl$_4$/SiH$_4$ partial pressure ratio varying from 0.04 to 0.4. The microstructure and the transport properties of the films were studied as function of the substrate temperature in the range 400-500°C. An annealing step at 800°C was also required to obtain a low resistivity.

Tantalum disilicide, TaSi$_2$

The reported works on TaSi$_2$ include the exclusive use of tantalum chlorides and
silicon-bearing molecules in the three basic systems: APCVD (22, 25), LPCVD (40, 23, 51, 55), and PECVD (56).

The first work on the CVD of this material for IC manufacturing comes from Lehrer et al (51, 52) using a multi-wafer LPCVD hot-wall reactor in a temperature range of 500-650°C, a pressure of 0.3 torr and various TaCl₅/SiH₄ gas flow rate ratios. A polycide structure was produced by sequentially depositing poly-Si and Ta₅Si₃ in a single process. The Ta₅Si₃ was then converted to TaSi₂ by heat treatment either outside (51) or inside the reactor (52).

Similar processes and results have been described by Williams et al (53) and Widmer et al (54). However, using the same kind of LPCVD system, Bouteville et al (40) reported the direct deposition of TaSi₂ on silicon substrate starting from the same chemical species and a similar temperature range. No satisfactory explanation of this discrepancy has been proposed so far.

Using now a cold-wall single wafer LPCVD system, a TaCl₅ solid source, silane and hydrogen, Wieczorek et al (28) demonstrated that TaSi₂ films could be formed directly in a temperature range of 630 to 750°C at a deposition rate of 70 nm.min⁻¹ with a minimum resistivity of 60 μΩ x cm, after annealing for one hour at 900°C in argon.

A similar process has been described by Reynolds (23) using a mixture of SiH₄, TaCl₅, H₂, HCl and Ar at pressure between 100 mtorr and 1 torr over the temperature range 620-700°C. The compositions of the films could be controlled by adjusting the deposition temperature, total pressure and the partial pressures of reactant gases. A thermodynamic analysis of the deposition process was performed but the results have not been published so far. TaSi₂ films with good adhesion were deposited on Si and SiO₂ and as deposited resistivity values as low as 55 μΩ x cm were achieved at a deposition temperature of 700°C.

A different approach has been used by Hieber et al (56) to deposit tantalum silicide films at low temperature in a PECVD system. An inductively generated plasma was applied to a mixture of TaCl₅, SiH₂Cl₂ and H₂ at an overall pressure of about 2 mbars and a substrate temperature above 400°C. Up to a substrate temperature of 540°C the films were amorphous after deposition whereas above 580°C crystalline TaSi₂ has been produced with a resistivity of about 70 μΩ x cm. A further drop of the resistivity to about 55 μΩ x cm was obtained after annealing these films 1 hour at 900°C in argon.

Starting from an equilibrium thermodynamic calculations of the CVD diagrams for the system Ta - Cl - H - Ar - Si, we have recently defined the experimental conditions leading to TaSi₂ system by APCVD (25). Based on these calculations, high quality TaSi₂ films have been deposited on both Si and SiO₂.
in cold wall reactor working at atmospheric pressure, using silane and tantalum chlorides produced in situ by the reaction of chlorine on tantalum maintained at 550°C (figure 2). Experiments were carried out at temperatures between 600 and 850°C. Below 680°C, no deposition occurred. Gas phase compositions were chosen in order to obtain films with different Si/Ta ratios from 0.7 (TaSi2 + Ta5Si3) to 2.6 (TaSi2 + Si) according to the calculated phase diagrams. Deposited films of TaSi2 are 200-2000 nm thick, have a surface roughness of below 15 nm, a plane substrate-silicide interface and a resistivity lower than 70 μΩ x cm after annealing at 900°C for 2 hours.

Fig. 2: Schematic representation of the APCVD experimental set up for TaSi2: 1 quartz tubes, 2 graphite susceptor, 3 rf heating, 4 resistance heating, 5 Ni-Cr thermocouples, 6 tantalum bed, 7 gas inlet, 8 gas mixing, 9 gas outlet, 10 gas products neutralization, 11 vacuum

Tungsten disilicide: WSi2

Films of tungsten disilicide have been obtained by APCVD (29, 57, 58) LPCVD (7, 19, 20, 59-64) and PECVD (65) using almost exclusively a mixture of WF6 - SiH4 and H2 with or without a neutral carrier gas. Only one study of the CVD of WSi2 starting from WCl6 has been reported so far by Lehrer et al (57). Bilayer films of Si and WSi2 were obtained at 600°C by sequential deposition of Si and W using SiH4/N2 and WCl6/H2 mixtures at atmospheric pressure. During the W deposition, a crystalline WSi2 layer grows on the Si layer with grain size in the order of 10 nm. After anneal, the grain size is 30-50 nm and the electrical resistivity as low as 65 μΩ x cm.
However, the first reported work on the APCVD of WSi₂ by Lo et al (29) makes already used of the commercially available and easy to handle tungsten hexafluoride WF₆.

Just after Lehrer's work, was reported a study of the deposition of WSi₂ by PECVD (65) using also a mixture of WF₆ and SiH₄ in a rf parallel plate reactor at 13.56 Mhz, a substrate temperature of 230°C and a pressure of 0.5 to 0.7 Torr. The atomic ratio of W/Si in the film depended on the WF₆/SiH₄ gas flow rate ratios. Most of the deposited films were amorphous and a high temperature annealing step was used to lower their resistivity.

Soon after Brors et al (17,19,20) reported the deposition of WSi₂ in a cold wall multiwafer LPCVD system. Deposition were done on Si and SiO₂ in a temperature range of 300 to 450°C and a pressure range of 0.1 to 0.3 torr. In these ranges, the deposition rate was found to be independent of temperature and pressure, independent of SiH₄ flow rate; however, a linear function of WF₆ flow rate. Any change in the WF₆/SiH₄ gas flow rate ratio causes a corresponding change in the Si to W ratio in the deposited films.

This can be understood easily, looking to the CVD phase diagram calculated recently for this system (15), and represented in figure 3. The WSi₂ domain is reduced to a single line; so, any deviation of the WF₆/SiH₄ gas flow rate ratio from the ideal composition corresponding to WSi₂ must produce mixed phases films, going from W₅Si₃ + WSi₂ to WSi₂ + Si.

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**Fig. 3**: Computed equilibrium "CVD phase diagram" in the system W-Si-H-F-Ar for the following experimental parameters: total pressure 1 atm, deposition temperature 720°C, argon partial pressure: 0.9
Despite this problem, this LPCVD process has been considered as a reference in the field of CVD of WSi$_2$ and most of the works reported after concerned almost exclusively the characterization of films obtained by this technique (64, 66-68).

**Molybdenum disilicide MoSi$_2$**

There have been only few reported studies of the CVD of MoSi$_2$ for IC manufacturing, all using a LPCVD system.

The first report comes from Inoue et al (24) using a LPCVD hot wall multi wafer reactor at a pressure of 0.6-2 Torr and in a temperature range of 520-600°C. Silane was used as the silicon source and MoCl$_5$ as the metal source. MoSi$_2$ films were deposited at low temperature (670°C) onto oxidized Si substrates. An annealing step at temperatures between 700-1000°C was needed to reduce the resistivity of the as-deposited films to its usual value (60-100 $\mu$Ω x cm).

The other reports on the LPCVD of MoSi$_2$ (27, 62, 69, 70) deal with the reaction of MoF$_6$ with silane in the presence of hydrogen in cold wall reactors. The LPCVD of molybdenum silicides was observed at temperature as low as 150°C, some 200°C lower than LPCVD WSi$_x$. The reported results are similar to those obtained previously for WSi$_x$ made by the reaction of WF$_6$ and SiH$_4$ with at least one main difference: the composition of the deposited films depends only on the deposition temperature for a wide range of MoF$_6$/ SiH$_4$ gas flow rate ratio.

We have not performed yet thermodynamic equilibrium calculations in the system Mo - Si - F - H - Ar. But for obvious reasons, we suspect that the CVD phase diagram for this system must be very similar to the one calculated for W - Si - F - H - Ar system. The reported difference in the sensitivity of the deposited film composition to the reactive gases flow rate ratio may be attributed to some kinetic effect which must be studied to get a better understanding of these processes.

**FUTURE DIRECTIONS IN CVD OF METAL SILICIDES**

Today VLSI technology is moving into the ULSI era in which the feature size of practical devices must be well into the submicron range. Like the CVD of dielectrics (71), the CVD of refractory metal silicides must make some accommodations as well.

The results reported so far in this paper concerned the deposition of "blanket silicide" mostly for polycide structure in conjunction with a predeposited poly-silicon layer. As regards to the materials
requirements for the new generation of ULSI devices, it must be extremely important to use silicides also as contacts for the source and drain regions in addition to the gate. One solution which is investigated is the salicidation process in which the metal deposited by a PVD technique is reacted onto Si/SiO₂ patterned wafer to form the metal silicide only on the bare silicon surface. This has been achieved for example with TiSi₂ (72). However, this method requires in this case a titanium and titanium nitride strip and an annealing step after the TiSi₂ film is formed. Moreover the salicide process implies the consumption of the underlying silicon and thus is not compatible with the fabrication of shallow junctions.

This salicide process may be replaced in the near future by selective CVD of the metal silicide. Several attempts have been made in order to set up a selective deposition process of TiSi₂ based on the silicon reduction of TiCl₄ in the presence of hydrogen (21). But there was still a consumption of silicon from the substrate which may cause reliability problems. One solution to this problem which is presently investigated is the use of a reactive mixture containing a silicon bearing molecule.

Two selective deposition processes of TiSi₂ have been reported recently, using both a mixture of TiCl₄ and SiH₄. The first one reported by Ilderem et al (73, 74) makes use of a thin polysilicon layer deposited prior to the silicide in a cold-wall very low pressure CVD reactor. It is shown that selective deposition is possible by controlling the polysilicon and the titanium silicide deposition times. But even at a deposition temperature as low as 730°C, 40% of the silicon in the titanium silicide film originates from the consumption of the underlying silicon substrate. The process is based on the etching and/or consumption of the thin polysilicon layer due to the deposition chemistry which has not been explained further yet.

In fact, all the results obtained so far in the selective deposition of this material by CVD may be explained by the presence of a native oxide layer on the surface of the silicon substrate which prevents the nucleation of TiSi₂. Based on this assumption, three solutions may be considered for a selective deposition of this material:

- A classical etching step prior to deposition, by reacting the substrate with a gas mixture of H₂/HCl at 1100°C.
- The selective deposition of silicon prior to the deposition of TiSi₂ in a LPCVD reactor, leading to a selective polycide structure.
- Or the solution we have investigated, namely the use of an appropriate choice of the reaction gas (TiCl₄, SiH₄, H₂, Ar) for an in situ etching of the native oxide at the beginning of the deposition process (74, 75).
Indeed thermodynamic equilibrium calculations performed in this system show that a slight excess of silane in comparison with the composition leading to the formation of TiSi$_2$ converts SiO$_2$ into volatile SiO with a significant yield above 900°C at atmospheric pressure (75). Starting from these calculations, selective deposition of TiSi$_2$ has been obtained recently at temperature as low as 700°C, in conformation with the design down to 1 μm size patterns (74). An example of selective deposition on patterned wafer is given in figure 4.

Fig. 4: SEM micrograph of selective titanium disilicide deposited on patterned silicon wafer. TiSi$_2$ line width: 4 μm.

Successful selective deposition of metal silicide was also obtained by Hieber et al. in the case of TaSi$_2$ (76, 77) according to the reaction chemistry:

$$2 \text{ SiH}_2\text{Cl}_2 + 5\text{H}_2 + 2\text{TaCl}_5 \rightarrow 2\text{TaSi}_2 + 18\text{HCl}$$

This method requires adjusting the substrate deposition temperature and composition of the reaction gas to values at which silicide nucleation in regions of the substrate other than silicon regions is suppressed during deposition from the gaseous phase due to the presence of the hydrogen halide. The deposition temperature were between 600°C and 800°C and the deposition pressures ranged from 0.5 mbar to 1 mbar. No consumption of underlying silicon was detected by TEM examinations. This process may be of great potential in the metallization of shallow junctions in submicron IC structures, once solved the problem of the surface roughness of the deposited films.
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