PROCESSING OF WSi_2 FILMS BY LOW PRESSURE CHEMICAL VAPOR DEPOSITION FROM IN SITU CHLORINATION OF METAL

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Abstract - An experimental investigation of WSi_2 thin films by LPCVD from in situ elaborated metal chlorides is presented. The films composition and properties are studied as a function of input gas phase composition. Preliminary results show that WSi_2 films can selectively grow on silicon. An attempt has been made to understand the results in terms of deposition conditions.

1.-Introduction.

As the feature of VLSI circuits continues to shrink below one micron, unmet requirements have driven industry to find alternative methods to achieve acceptable RC delay due to interconnection paths and to manage wafer topography issues. Because CVD tungsten and tungsten disilicide, WSi_2 , meet these requirements and offer diffusion barriers and improved electromigration resistance, the level of interest in this technology has mushroomed. At present the CVD WSi_2 films are mainly processed by fluorine based reactive gases. However, additionally to the technical problems due to the high reactive nature of these gases, this process is rather delicate to optimize.

An alternative solution may be the use of chlorides instead of fluorides as tungsten precursors. We have already illustrated the advantages of the chlorides by doing a comparative thermodynamic study of the two processes /1/. We have proposed a controlled and reproducible way of production and transport of the tungsten chlorides. It consists of an in situ chlorination of a thermoregulated tungsten bed situated just above the substrate. We simulated and thermodynamically optimized the chlorination conditions and also analysed the resulting gaseous phase by mass spectrometry /2/. Based on these two works we presented a first experimental study of the CVD of WSi_2 at atmospheric pressure /3/. This study showed the feasibility of the deposition from the chlorides and the qualitative agreement between the calculated and the

experimental results. However, the oxygen contamination of the chlorinated metal due to the conception of the CVD reactor induced the presence of impurities and the codeposition of W and WSi_2 in the as deposited films.

Technical solutions for this problem combined with modifications in the operating conditions are presented in this work. The improved process for the CVD of WSi_2 is based as in our previous works on a thermodynamic simulation which now takes into account the precision of the adopted thermodynamic data for the implicated compounds. The outcomes of this simulation, the change to low pressure operating conditions and the first experimental results are presented. Finally the possibilities of integration of the process into a selectively deposited WSi_2 technology are discussed.

2.-Thermodynamics.

The thermodynamic investigation was realised using a computational method based on the minimization of the Gibbs free energy of the total system W-Si-Cl-H-Ar /4/. The compositions and the amounts of the deposited phases and of the gaseous by-products at equilibrium were calculated as function of the reactive gas phase composition, the total pressure and the temperature. The results are illustrated by means of CVD phase diagrams which indicate the nature of the deposited phases (tungsten silicides) as a function of two experimental parameters. In this case the CVD phase diagrams are drawn as a function of the initial partial pressures of the silicon and tungsten precursors, SiH_4 and WCl_4 respectively, WCl_4 being the main chlorination product in the adopted conditions /2/. Each CVD phase diagram is elaborated for a given operating temperature, pressure and Ar dilution. The H_2 partial pressure is obtained in each point of the diagram as the difference between the total pressure and the sum of the above mentioned partial ones. In this diagram two phase deposition domains alternate with one phase domains. Neighbour domains are separated by stripe type lines whose width is function of the precision of the thermodynamic data used in the calculations. More the involved species are thermodynamically well defined less the width of these limits is large. The systematic consideration of the precision of the used data, as was recently proposed by Thomas et al /5/, was realized by adjusting the minimization software in order to provide the width of the border lines for every calculation made at the limit of two neighbour deposition domains. In this way the reliability of the resulting predictions is increased. At the same time the species of the chemical system which need a more precise thermochemical description leading to the reduction of the width of the border lines are evidenced.

Figure 1 presents the CVD phase diagram drawn at the operating conditions of $T = 873\text{K}$, $P_{\text{tot}} = 133 \text{ Pa}$ (1torr), $P_{\text{Ar}} = 0.9 \cdot P_{\text{tot}}$ which give the best quality films obtained up to now. A systematic investigation of the influence of T , P_{tot} and P_{Ar} on the composition of the deposited films is in progress. In this diagram the points A...H correspond to different gas phase compositions. A zoom of the upper

Figure 1. CVD phase diagram in the W-Si-Cl-H system for the deposition from WCl_4 , SiH_4 and H_2 . $T = 873\text{K}$, $P_{\text{tot}} = 133\text{ Pa}$, $P_{\text{Ar}} = 0.9 \cdot P_{\text{tot}}$.

Figure 2. Zoom in the 10^{-3} to 10^{-2} mole fraction area of the CVD phase diagram of figure 1.

left area of this diagram is presented in figure 2. In order to better illustrate the width of the deposition domains in this part the zoom is drawn in linear coordinates. The zoom concerns the most interesting part of the diagram since there the WSi_2 deposition domain is larger. Moreover, as evidenced after the preliminary experiments, the precursors partial pressures in this area lead to satisfactory growth rates of approximately 100 nm/min.

It can be noticed that the pure WSi_2 deposition domain is fairly limited compared to the extent of the precursors partial pressures investigated although it is larger than for the deposition from WF_6 in the same conditions. Its limits are better defined than the ones of the other domains.

3.-Experimental

Tungsten silicide thin films were processed in a vertical cold wall quartz reactor, previously described /6/. The reactor was additionally equipped with an Alcatel primary vacuum pump and a MKS regulation system including a baratron gauge, a throttle valve and an exhaust valve controller. The limit vacuum for 1 lt/min flow rate was 100 Pa. Chlorine was passing through the chlorination chamber filled with tungsten wires and heated by a lamp furnace at a fixed temperature of 1073K following the results of the corresponding theoretical investigation /2/. The amount of tungsten chlorides admitted into the reactor was controlled by the Cl_2 flow and the chlorination chamber temperature. The resulting WCl_4 rich gas phase was mixed with the other reactive gases above the deposition zone which contained the substrates lying on an inductively heated graphite susceptor. Prior to deposition the chlorination chamber was degassed at 133 Pa and 1073K under 150 cc/min of H_2 flow. Following the thermodynamic calculations /2/, the combined action of low pressure and hydrogen dissociates the solid tungsten oxychloride $\langle \text{WO}_2\text{Cl}_2 \rangle$ which is superficially formed in the chlorination chamber during the loading of the substrate.

The deposition conditions were the ones of the presented CVD phase diagrams. The purity of the gases was N55 except for Cl_2 for which it was N40. Starting silane was 1% diluted in argon. Deposition was made on (111) oriented boron doped silicon as well as on Si-SiO_2 patterned wafers (resistivity 10-20 Ω .cm) for fixed time of 10 min and total flow rate of 1000 cc/min. Before the silicide deposition a Si predeposition was performed with 5 cc/min of SiH_4 for 5 min at $T = 923\text{K}$ and $P_{\text{tot}} = 67$ Pa. The deposited films were annealed at $T = 1273\text{K}$ in 101.4 kPa of Ar for 120 min. The as-deposited and annealed films were characterized by SEM, Four Point Probe, X-Ray Diffraction, AES and profilometry. Table 1 presents the flow rates of the Ar, SiH_4 , H_2 , Cl_2 and the produced WCl_4 , assuming a complete transformation of the chlorine to WCl_4 , for the experimentally investigated points A to H which are reported in figures 1 and 2.

Table 1. The reactive gases flow rates in cc/min for the different operating conditions investigated.

Total flow rate 1000 cc/min, $T=873\text{K}$, $P_{\text{tot}}=133\text{ Pa}$

	A	B	C	D	E	F	G	H
SiH ₄	5	0.8	2	9.8	5	5	5	5
Cl ₂ (WCl ₄)	3 (1.5)	3 (1.5)	3 (1.5)	5 (2.5)	10 (5)	4 (2)	6 (3)	5 (2.5)
H ₂	92	97	95	20	85	91	89	90

4.-Results.

The initial operating conditions in our study were these of the point A. They correspond to a codeposition of almost pure WSi₂ with some Si. This choice was based on the results of a similar investigation on the Ti-Si system which showed that the first steps of the reaction of the gas phase with the surface are facilitated by the presence of Si in the deposited films [7]. Based on this composition and in order to confirm the thermodynamic predictions, we fixed at 3 cc/min the Cl₂ flow rate and varied the SiH₄ one. However, the reduced concentration of SiH₄ near the B point lead to a very low and irreproducible growth rate. Consequently we fixed the SiH₄ flow rate and we varied the Cl₂ one thus moving along the A-E line.

In figure 3 are presented three typical X-Ray diffraction spectra of the as deposited films under the operating conditions of the points F, G and E. The revealed compositions correspond to the thermodynamically predicted ones. Silicon coming from the substrate is also present in the spectra. The X-Ray spectrum of the point A is identical to the one of the point F. It is thus not possible to verify in this way if Si is codeposited with WSi₂ in the A point conditions. It is worth noting that WSi₂ is obtained exclusively in its hexagonal form. Contrary to the results we reported for the APCVD of WSi₂ [3] neither tetragonal WSi₂ nor tungsten is obtained in these conditions indicating that the deposited films are oxygen free. The X-Ray diagram of the F point composition annealed films is presented in figure 4. It is exclusively composed of (001) preferentially oriented tetragonal WSi₂.

The AES analysis indicates no excessive carbon, chlorine and oxygen contamination.

The films morphology is affected by the composition. More the films are W-rich (ex. point E) more they are rough and show textured interface. On the contrary WSi₂ films are mirror like. Their surface roughness is below 10 nm while the silicide-silicon interface is planar as shown in the two SEM photographs of

figure 5. These characteristics do not change with annealing. Films with a thickness of less than $1.5\ \mu\text{m}$ present good adhesion to substrates.

Figure 3. X-Ray Diffraction spectra of as deposited films in three different operating conditions corresponding to the points E (spectrum a), G (spectrum b) and F (spectrum c) of the CVD diagram of figure 2.

Figure 4. X-Ray Diffraction spectrum of a WSi_2 film deposited in the operating conditions of the point F after annealing.

The resistivity of the as deposited WSi_2 films is about $1000\ \mu\Omega\cdot\text{cm}$. It decreases to about $100\ \mu\Omega\cdot\text{cm}$ after annealing.

The investigation of the selective deposition of the WSi_2 films is actually in progress. The preliminary results confirmed the selective behaviour of the $WCl_4\text{-SiH}_4\text{-H}_2$ system with regard to the nature of the substrate. Si predeposition is necessary for the growth of the films except for the deposition made in the $WSi_2\text{-Si}$ domain. Optimizing the Si predeposition conditions lead to the elaboration of selective films for each point E, F, G, H. The quality of these films depend on the Si content of the gaseous phase. For the deposition in the conditions of points F and H the Si/ WSi_2 interface is conserved but selectivity is delicate to achieve. Deposition in the conditions of the points G and E is

easier but results in the attack of the Si substrate as shown in the SEM micrograph of figure 6: In the presented Si-SiO₂ patterned wafer the SiO₂ part is not affected by the deposition. On the other hand porous silicide film has grown on silicon.

Figure 5. SEM micrographs of the surface (a) and the cross section (b) of a blanket WSi₂ film.

Figure 6. SEM micrograph of the surface of a Si-SiO₂ patterned wafer with the silicon parts covered by tungsten silicide.

It appears that the behaviour of the WCl₄-SiH₄-H₂ system towards the selectivity is equivalent to the well established TiCl₄-SiH₄-H₂ one as studied by Mastromatteo [7]. Following this author the appropriate choice of the operating conditions with regard to the TiSi₂/TiSi₂+Si limit in the corresponding CVD phase diagrams is essential in the selective process. This was confirmed in the tungsten based system since starting with a Si rich composition lead to a non selective deposition. However the interaction between the native oxide on Si with the chlorine containing gaseous species in the very first steps of the process must be elucidated in order to optimize the silicon predeposition as well as the silicide deposition conditions and achieve a reproducible selective deposition of WSi₂.

5.-Conclusions.

We have carried out an experimental investigation of tungsten disilicide Low Pressure CVD supported by an a priori thermodynamic simulation of the process. WCl_4 was produced in situ by passing chlorine through a heated pure tungsten bed. Submicronic blanket WSi_2 films were deposited at $T=873\text{K}$ and $P_{\text{tot}}=133\text{ Pa}$ from a gaseous phase composed of SiH_4 , WCl_4 , H_2 and Ar.

The films were deposited under operating conditions virtually the same as the ones predicted to be appropriate by the calculations. Their morphology and resistivity are compatible with the latest microelectronic technologies requirements.

We have shown that this chlorine containing chemical system has a selective behaviour with regard to the substrate nature. The investigation of the selective deposition of WSi_2 is now in progress.

6.-Acknowledgments

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