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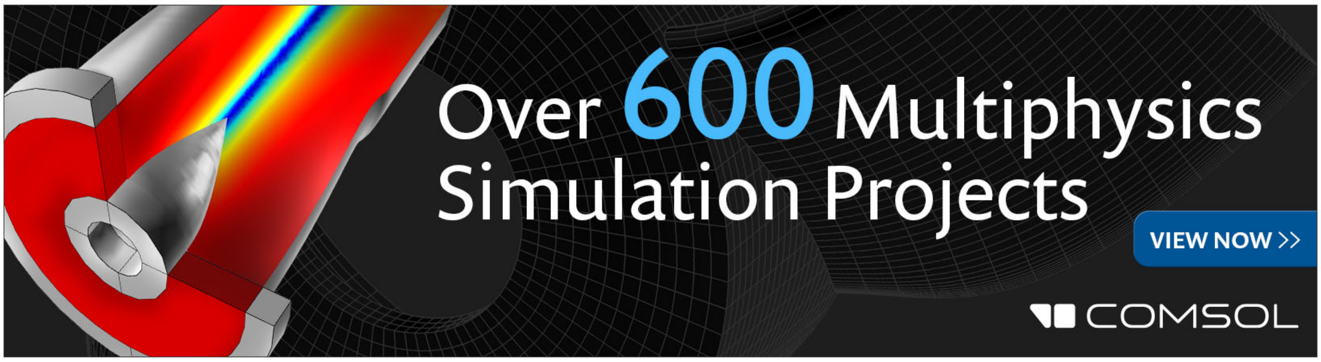

Kinetics aspects of $TiSi_2$ deposition without silicon consumption

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Selectively deposited layers of $TiSi_2$ have been obtained without Si substrate consumption using the $TiCl_4/SiH_4$ system diluted in H_2 at 800 °C. For a given set of parameters, we show that $TiSi_2$ formation uses Si coming from the substrate or from the gas phase, the principal parameters being the $TiCl_4/SiH_4$ ratio, the carrier gas, and gas mass transfer as the limiting mechanism of the reactions.

Selective deposition of metal silicides, among which $TiSi_2$ exhibits the lowest resistivity, is very likely to be used in future submicron silicon technology. Atmospheric,[1,2] low-pressure,[3,4] plasma,[5] or ultraviolet irradiation-enhanced[6] chemical vapor deposition (CVD) have been used. If small thicknesses required in future geometries are no longer a problem, on the other hand, silicon substrate consumption must be avoided in the $TiSi_2$ formation. Ilderem and Reif[4] proposed a two-step process: first depositing a polycrystalline silicon layer at 600 °C, then comsuming it by $TiCl_4$ at 730 °C.

In this letter we report for the first time selective deposition of $TiSi_2$ without Si substrate consumption in a short time (minute range) at 800 °C and under low total pressure (Torr range) using a mixture of $SiH_4/TiCl_4$ diluted in hydrogen, in a cold wall reactor, heating the silicon wafer by a fast-switching lamp system. It is shown that $SiH_4/TiCl_4$ diluted in H_2 shows relatively independent behaviors, the limiting mechanism being the mass transfer in the gaseous phase of the two species.

The experimental arrangement, similar to the original version of Gibbons *et al.*,[7] has been described elsewhere.[8] The addition of a separate line at the reactor entrance coming from a $TiCl_4$ saturator is the major modification. $TiCl_4$ injection is controlled, although its actual vapor pressure in the reactor is unknown, by the saturator temperature (here, room temperature) and an argon flow (5 sccm) bubbling in the liquid. The SiH_4 flow rate is 40 sccm. If these experimental parameters are close to those of Ilderem and Reif,[3] the striking difference in our case is the dilution of the species in a carrier gas either H_2 (2 slm) or a mixture of He and H_2 in equivalent amounts. All the reactions described in the following are made with the same set of parameters: $SiH_4/TiCl_4$ flows diluted in carrier gas, same total pressure of 2 Torr, temperature and deposition time (1 min). Deposition is carried out on (001) silicon wafers. Prior to the process, an oxide layer was patterned in parallel stripes, alternative oxide ($8\,\mu m$) and Si windows ($12\,\mu m$). This structure, obviously useful for selectivity study, is also basic for kinetic studies. Indeed, $TiSi_2$ thickness is deduced from two successive stylus profiling measurements. One just after selective deposition gives the height difference between the top surface of $TiSi_2$ and SiO_2, and the other, after removal of SiO_2 and $TiSi_2$ by HF, gives the height difference between the bottom of $TiSi_2$ and the location of the Si-SiO_2 interface. As-deposited $TiSi_2$ layers are polycrystalline, single-phase, stoichiometric $TiSi_2$, and exhibit the stable C54 structure as measured by x rays. The composition was also analyzed by in-depth Auger electron spectroscopy (AES) and Rutherford backscattering (RBS) profiling; the Si/Ti ratio is 2. These same techniques also determine the composition of pedestal structure (below the $TiSi_2$ layer) when existing as shown later. Moreover, $TiSi_2$ resistivity measured by four probe without any further thermal treatment ranges from 15 to $20\,\mu\Omega$ cm. Surface roughness at the $TiSi_2$/Si interface is typically 200–300 A peak to peak.

Experimental data are gathered in Table I; the only variable is the ambient in the reactor. The first column is the run names, from *R*-1 to *R*-4. The second column represents, for each case, the reacting and/or inert gases involved. In the third column, we emphasize the selectivity of the deposition, i.e., no nuclei at all are observed over the oxide (Fig. 1). The last two columns correspond to the thickness of the $TiSi_2$ formed using either a Si substrate (consumption) and/or Si from the gas phase ("true" deposition). Selectivity is easily explained by the important HCl production during the reactions. In all four runs studied, the constant species are SiH_4 and $TiCl_4$, so $TiCl_4 + 2SiH_4 \rightarrow TiSi_2 + 4HCl + 2H_2$ and Si(adsorbed on the oxide) $+ 2HCl \rightarrow SiCl_2(g) + H_2$. At this reduced pressure, the silicon nuclei etching by HCl is very active and therefore so is the formation of volatile species, as already shown.[9] For *R*-1, $TiCl_4$ and SiH_4 are involved. In

TABLE I. Systems tested at $T = 800$ °C during 1 min with the amounts of $TiSi_2$ formed. The gas flow ratios are the same for all the systems. "Select." refers to selectivity on oxide. "Consump." and "deposited" refer to $TiSi_2$ formed from Si substrate consumption and from species in the gas phase, respectively. In *R*-1 and *R*-4, the Si layer is the pedestal for the $TiSi_2$ layer. Pressure: 2 Torr, temperature: 800 °C; process time: 1 min, $TiSi_2$ (A/min).

No.	Reactions	Select.	Consump.	Deposited
R-1	$TiCl_4 + SiH_4$	Yes	0	450 $TiSi_2$ on 1050 Si
R-2	$TiCl_4 + H_2 + SiH_4$	Yes	0	1700
R-3	$TiCl_4 + H_2 + HCl + SiH_4$	Yes	1200	200
R-4	$TiCl_4 + SiH_4 + (He + H_2)$	Yes	0	1500 $TiSi_2$ on 1200 Si

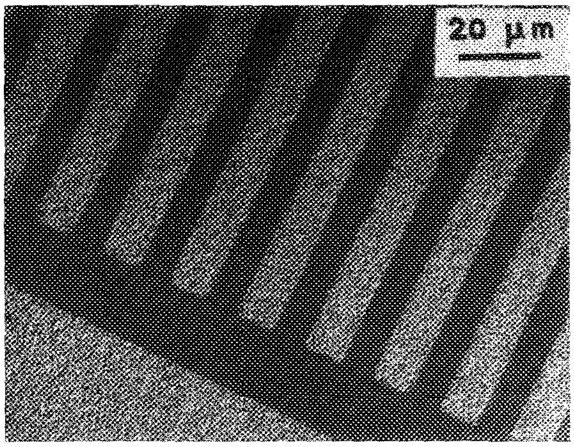

FIG. 1. Optical micrograph in Nomarski mode showing the selectivity deposited $TiSi_2$ without substrate consumption on patterned wafers. The dark regions are the oxide. Periodicity is 20 μm.

this case only the total pressure is lower than 2 Torr. For *R*-2, H_2 is added for a dilution of the species down to 1%. For *R*-3, H_2 plus 1:1000 volumetric ratio HCl are used. In *R*-4, a (H_2 + He) 50:50 partial pressure mixture at 2 Torr constitutes the carrier gas. 800 °C was selected because, as we see in *R*-2, we achieved our goal of $TiSi_2$ formation without Si substrate consumption. Below 800 °C, deposition of $TiSi_2$ layers without substrate consumption can take place but the deposition conditions are more critical. At 900 °C, the *R*-2 condition gave a deposited $TiSi_2$ thickness only slightly higher than that at 800 °C.

As seen from the qualitative results in Table I, the question arises to determine the rate-limiting step for $TiSi_2$ formation. Apparently, from *R*-1 and *R*-4, the reacting system as a whole can be characterized by an excess of silicon source compared to the titanium source. *R*-2 instead exhibits conditions for the right balance and *R*-3, on the contrary, gives rise to a deficiency in the external Si source. Unfortunately, the weak influence of temperature on the result cannot help us to discriminate between mass transfer and reactional processes on the basis of an apparent activation energy, which turns out to be weak in this system. In *R*-2, the ratio between $TiCl_4$ and SiH_4 is critical; this can be vividly enlightened by changing the SiH_4 injection by $\pm 50\%$ around its right value. At the lower injection (20 sccm), Si substrate consumption takes place, and at the highest one (60 sccm), a Si pedestal below $TiSi_2$ is formed as checked by AES and RBS. The consumption case demonstrates that $TiCl_4$ does not distinguish between the Si substrate and the SiH_4 as silicon sources; this is a clue for a limitation related to the actual $TiCl_4$ supply to a reacting front, instead of a chemical limitation of its reactivity.

We now come to a kinetic picture of a relative independence of SiH_4 and $TiCl_4$ behaviors (to be more general than pure chemical activity). Because of the large difference in mass, and therefore, in diffusivity and thermal conductivity of these primary sources, their molecular diffusion[10] towards the heated surface induces striking differences in their actual supply, even though the nominal injection levels are sufficient. These differences can probably be exemplified by (i) thermal diffusion effects in the existing strong thermal gradient (hot sample–cold wall), and (ii) their thermal accommodation to the reacting surface. In our opinion, this is why the $TiSi_2$ formation is so sensitive to the dilution conditions, determined by either an inert gas (He) or by a secondary reacting species (H_2 with or without HCl). As an example, if we compare *R*-2 and *R*-4, we have the same $Ti(Cl_4)$ supply, but it results in different final situations. However, these results can be almost wholly explained from what we know from the $SiH_4/H_2/He$ system alone using the same reactor.[9] In *R*-4 indeed, the total Si utilized for $TiSi_2$ formation is roughly 2550 A if we assume that the pedestal structure is almost composed of silicon. This value is close to 1.5 times that of the Si used in *R*-2 for the $TiSi_2$ formation. This Si ratio of 1.5 fits nicely with our results reported elsewhere[9] for the $SiH_4/H_2/He$ system in the study of the growth rate as a function of the hydrogen partial pressure. Furthermore, the smaller absolute amount of Si involved in the $TiCl_4/SiH_4$ experiments (*R*-2, *R*-4) compared to the case of the abovementioned system is obviously due to volatile chloride formation. A stoichiometric description of these reactions has been previously reported.[11]

R-3 appears more intricate. At first glance, it seems very astonishing that a small HCl addition can bring about such a dramatic change as compared to *R*-2. Indeed, the total $TiSi_2$ thickness is moderately reduced to 80% of the *R*-2 value, but these 1400 A $TiSi_2$ are nearly totally provided by the Si substrate. This inhibition of silane reactivity (for $TiSi_2$ formation) does not agree at all with our results obtained in the $SiH_4/H_2/HCl$ system using the same reactor.[9] For very similar conditions, a decrease by a factor of 0.5 of the Si growth rate is observed by HCl addition. We measured the growth rate for the two systems SiH_4/H_2 and $SiH_4/HCl/H_2$ as a function of the temperature in these very reactor and pressure conditions.[9] The addition of HCl (10% of the SiH_4 concentration) drops the growth rate to just one half at 800 °C. This is in contrast with the drastic deposited layer thickness reduction observed in *R*-3. Some other chlorinated and volatile species should be included in our model. In the following overall reaction in which $TiSi_2$ formation must be present as well as volatilized chlorinated species in order to take into account the disappearance of Si from silane[3]:

$$TiCl_4 + 3SiH_4 \rightarrow TiSi_2 + SiH_3Cl + 3H_2 + 3HCl; \quad (1)$$

applying Le Chatelier's principle, the reaction should be driven to the left by the addition of HCl. This would bring about the observed reduced $TiSi_2$ formation and at the same time, a reduction in SiH_3Cl formation, which is not observed in *R*-4 since all the Si necessary for $TiSi_2$ formation is taken from the substrate and not from the gas phase.

In order to reconcile the previous results, the following kinetic picture implying a rate limitation of the Ti-bearing species transport towards the reacting front is proposed, explaining selectivity as well. The injection of $TiCl_4$ is sufficient indeed, but for instance, in the reaction:

$$H_2 + TiCl_4 \rightarrow TiCl_2 + 2HCl, \quad (2)$$

$TiCl_2$ can be considered as the actual source and HCl as an etching species which diffuses as rapidly as SiH_4 towards the

Si and SiO_2 surfaces. Silane dissociation takes place, giving rise to selective deposition over SiO_2, because HCl from $TiCl_4$ is rapidly available to etch away the labile silicon nuclei whose creation rate is reduced, but not inhibited. The slower $TiCl_2$ then arrives in contact with this last silicon to produce $TiSi_2$ and some silicon chlorides. The addition of HCl (R-3) does not change this mass-transfer limitation, however, the actual concentration of HCl including the added part and that (slightly reduced) coming from Eq. (2) has, relative to R-2, increased in such a proportion that now silane dissociation is truly inhibited. Due to this, the silicon substrate becomes the only Si source, and it cannot be etched by HCl at this temperature.

In conclusion, selective deposited layers of $TiSi_2$ without substrate consumption have been achieved using a rapid thermal process under reduced pressure in the $SiH_4/TiCl_4/H_2$ chemical system. A model involving gas mass transport of $TiCl_4$ as the rate-limiting step and assuming a relative independence of silane chemistry fits the experimental results well. More details and chemical reactions involved will be published elsewhere.[12]

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