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〈연구논문〉

PECVD of Blanket $TiSi_2$ on Oxide Patterned Wafers

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산화막 패턴 웨이퍼 위에 플라즈마 화학증착법을 이용한 균일 $TiSi_2$ 박막형성에 관한 연구

이 재 갑

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Abstract—A plasma has been used in a high vaccum, cold wall reactor for low temperature deposition of C_{54} $TiSi_2$ and for in-situ surface cleaning prior to silicide deposition. SiH_4 and $TiCl_4$ were used as the silicon and titanium sources, respectively. The deposited films had low resistivities in the range of 15~25 uohm-cm. The investigation of the experimental variables' effects on the growth of silicide and its concomitant silicon consumption revealed that SiH_4 and $TiCl_4$ were the dominant species for silicide formation and the primary factors in silicon consumption were gas composition ratio and temperature. Increasing silane flow rate from 6 to 9 sccm decreased silicon consumption from 1500 A/min to less than 30 A/min. Furthermore, decreasing the temperature from 650 to 590℃ achieved blanket silicide deposition with no silicon consumption. A kinetic model of silicon consumption is proposed to understand the fundamental mechanism responsible for the dependence of silicon consumption on SiH_4 flow rate.

요 약—C_{54}Ti-silicide($TiSi_2$)의 증착 온도를 낮추고 챔버내에서 표면처리를 가능하게 하기 위하여 플라즈마를 고진공장치에 부착시켰다. SiH_4와 $TiCl_4$를 이용하여 증착시킨 Ti-silicide는 14~25 uohm-cm의 낮은 저항을 가지고 있었다. 실험변수가 silicide의 성장속도와 이 때 발생하는 기판 실리콘의 소모(Silicon Consumption)에 미치는 영향에 대한 연구는 SiH_4가 실리사이드 형성에 참여하는 주요한 성분이며, 기판 실리콘은 silicide 형성에 참여하지 않고 소모됨을 보여주고 있었다. 또한 실리콘 소모에 주요한 영향을 미치는 인자는 가스조성과 증착온도였다. SiH_4를 6 sccm에서 9 sccm으로 증가시켰을 경우는 실리콘 소모가 1500 Å/min에서 30 Å/min 이하로 감소하였고, 온도를 650℃에서 590℃로 낮추었을 경우에는 실리콘 소모가 일어나지 않고 균일한 두께의 $TiSi_2$가 형성되었다. 마지막으로 기판 실리콘 소모에 SiH_4가 미치는 영향을 이해하기 위하여 실리콘 소모에 대한 반응 모델을 고려하였다.

1. Introduction

As the device dimension has been scaled down to submicron, the series resistance contributed by the source-drain ohmic contacts increases more rapidly than other series resistance components[1]. As a result, to take advantage of the enhanced performance obtained by device miniaturization, source-drain ohmic contact resistance and gate resistance must be minimized in addition to source-drain resistance. Refractory silicides of transistion metals have been used in MOS VLSI applications

to reduce the sheet resistance and to improve the source and drain contact resistance since they have low resistivity, high temperature stability, and good adherence[2, 3]. Among all the refractory metal silicides, titanium silicide is of particular interest due to its lowest resistivity, reasonable thermal stability, and demonstrated contact metallurgy, thus providing reliable low resistance contacts to shallow junctions[4].

$TiSi_2$ can be formed by the physical vapor deposition (PVD) or by the chemical vapor deposition (CVD) technique. Sputtering and evaporation are two PVD techniques which are widely employed for deposition of metal silicides. However, the poor step coverage of PVD process limits their application for small contacts having high aspect ratios. CVD processes offer the advanatages of excellent conformal coverage.

CVD of $TiSi_2$ has been accomplished by several methods with varying degree of success. The methods include: Atomospheric Pressure CVD (APCVD)[5], Low Pressure CVD (LPCVD)[6-10], and Plasma Enhanced CVD (PECVD)[11]. However, all these methods suffered from three basic problems: narrow deposition variable window, excessive silicon consumption, and the presence of native oxide.

In this study, Plasma Enhanced CVD was used to enlarge the deposition variable window, especially deposition temperature and to facilitate hydrogen plasma cleaning of the surface prior to silicide deposition, thus achieving a better control of the process. By utilizing plasma cleaning and the large deposition variable space available with PECVD, we have investigated the effects of deposition variables on the growth of silicide films and silicon consumption and determined the limiting steps and species in silicide formation. A kinetic model of silicon consumption is proposed to explain how SiH_4 gas flow rate effects silicon consumption. This model was confirmed by depositing blanket silicide on oxide patterned wafers with no silicon substrate consumption at 590℃ and at $SiH_4/TiCl_4$ flow ratio of 8/4 (sccm).

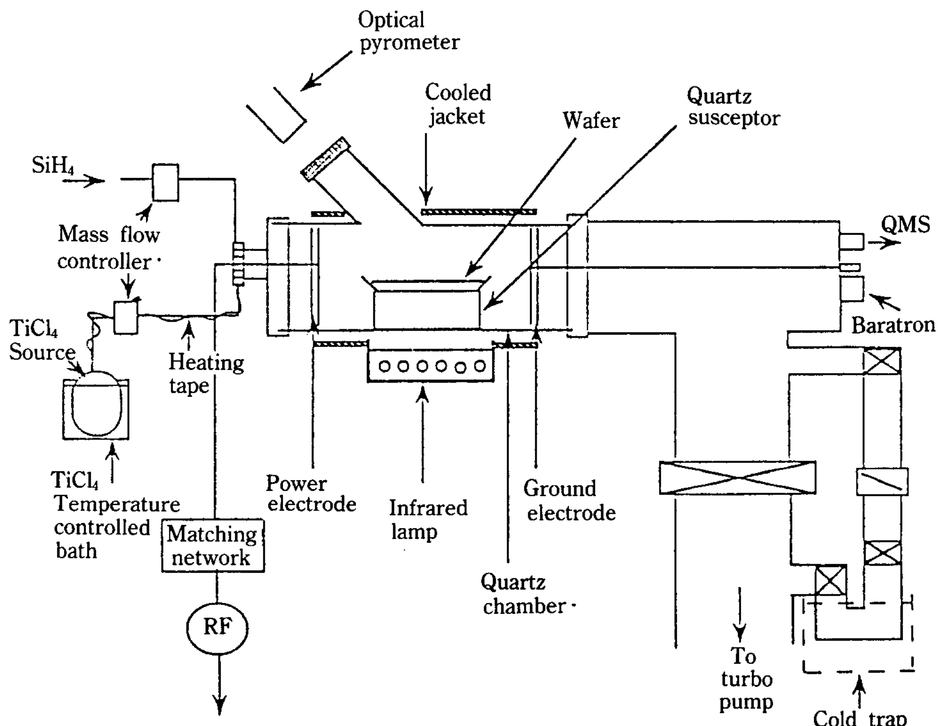


Fig 1. Schematic of the silicide reactor.

2. Experimental

2.1. Deposition system

The schematic diagram of the high vacuum PECVD silicide reactor is shown in Fig. 1. A turbomolecular pump, whose pumping speed is 510 l/sec, is used to obtain a base pressure of $<1\times10^{-7}$ Torr with the gate valve open. SiH_4 and $TiCl_4$ were used as silicon and titanium sources, respectively. The flow of gases in the reactor is controlled by mass flow controllers. The mass flow controller (MKS) of $TiCl_4$ was specially designed to avoid the need of a carrier gas to inject $TiCl_4$ into the chamber and avoid a surge of gas flow at the opening of the valve. A quadrupole mass spectrometer (QMS) connected to the rear of the chamber was used for detecting by-product gases as well as monitoring the tightness of the system. The pressure inside the chamber was monitored by a capacitance manometer during the deposition. During the silicide deposition, the gate valve was closed and a pressure control arm was used as a pumping line to install a cold trap (−70℃) along the line. Unreacted $TiCl_4$ gas condenses on the inner tube of the cold trap, preventing its attacking the turbopump.

The temperature of a single wafer sitting on a four-pin quartz susceptor was monitored by an infrared pyrometer through a saphire window. A bank of 6 lamps was designed to directly heat a single wafer utilizing maximum electrical power effectively, which facilitated abrupt changes in the wafer temperature. This was desirable to quickly switch from in-situ plasma cleaning at 650℃ to a deposition temperature.

The RF power supply was a 500 W, 13.56 MHz generator coupled through an automatic matching network to a 14 cm diameter power electrode spaced 20 cm apart from the grounded electrode. The wafer sitting on the quartz susceptor was electrically isolated. The plasma allowed in-situ hydrogen plasma cleaning prior to a titanium silicide deposition as well as a PECVD of silicide. The electrical isolation of the wafer in contact with the plasma allows a high flux of reactive radicals to the wafer surface under conditions of minimal ion bombardment which favors the formation of a stable titanium disilicide.

Table 1. Deposition conditions investigated for PECVD of $TiSi_2$

Variables	H_2 plasma cleaning	Titanium silicide
Temperature (℃)	650	550~780
SiH_4 flow (sccm)		5~10
$TiCl_4$ flow (sccm)		2~7
H_2 flow (sccm)	30	5~30
Argon flow (sccm)		5~15
Pressure (mTorr)	55	37~83
Deposition time (min)	40	1~10
Power (watts)	15	5

Table 2. Partial pressure of gases (a) for a cold base pressure and (b) for a hot base pressure

Species	Partial pressure (Torr)	
	(a)	(b)
H_2O	$\sim5.5\times10^{-8}$	$\sim3.3\times10^{-7}$
H_2	$\sim3.6\times10^{-8}$	$\sim1.6\times10^{-7}$
N_2	$\sim3.1\times10^{-9}$	$\sim5\times10^{-9}$
O_2	$<10^{-9}$	$<10^{-9}$
HCl	$<10^{-9}$	$\sim8.2\times10^{-9}$

2.2. Experimental procedure

Deposition was carried out on 100 mm, n-type, 2-5 ohm-cm, (100) silicon wafers under the conditions summarized in Table 1 for the deposition of blanket silicide on oxide patterned wafers. Wafers with a 1000 A (or 5000 A) thermally grown oxide were patterned. The oxide patterned wafer was cleaned in an RCA procedure followed by dipping into a 50 : 1 HF solution to remove the chemically grown oxide layer. The wafer was rinsed, dried, and placed the Ultra-Violet/Ozone Cleaning (UVOC) system to remove carbon and to grow a passivating oxide. The clean wafer was moved directly from the UVOC system into the chamber.

After loading the wafer, the chamber was pumped down to a "cold" base pressure of 1×10^{-7} Torr. The wafer was heated to deposition temperature and the chamber baked in argon to achieve a "hot" base pressure of 5×10^{-7} Torr. From the QMS data, it

was revealed that H_2O was the dominant component of the "hot" base pressure and the "cold" base pressure. Table 2 summarized a typical set of species detected by the QMS and their corresponding partial pressure for a "cold" and a "hot" base pressures. It is evident that baking the reactor even in the cold wall system helped to evaporate H_2O and HCl from the wall and the electrodes. The deposition procedure consisted of an in-situ hydrogen plasma cleaning of the passivating oxide followed by a PECVD step. $TiSi_2$ film deposited on oxide patterned wafers was characterized by using the following analysis tools.

The thickness of silicide films was measured by the surface profilometer. Cross-Sectional Transmission Electron Microscopy (XTEM) was used to assess the crystalline quality of silicide film. Glancing angle X-ray diffractometry was used to determine the phases and the degree of the preferred orientation of the deposited films. Scanning Electron Microscopy (SEM) was used to study the surface morphology and Auger Electron Spectroscopy (AES) to detect impurities such as carbon, oxygen, and chlorine in the silicide films. Rutherford Backscattering Spectroscopy (RBS) spectra taken using 2 or 3 Mev He^{2+} at normal incidence and 4° scatteing angle determined the stoichiometry of the films. The sheet resistance of the silicide was measured using a four point probe.

3. Results and Discussion

3.1. Growth rate

Growth rate experiments were conducted at varying temperatures, times and gas flow rate ratios. Typical duration time was 3 minutes. Fig. 2 shows the growth rate of titanium silicide deposited on silicon window (open circle) and on silicon dioxide (closed circle) as a function of temperature. For both substrates, there are two distinct regions of deposition rates. Region 2, at higher temperatures, is only slightly temperature activated. At lower temperatures (region 1), the growth rate shows a strong temperature activation. In an attempt to reduce the effect of temperature variations on silicide growth rate, the dependence of the growth

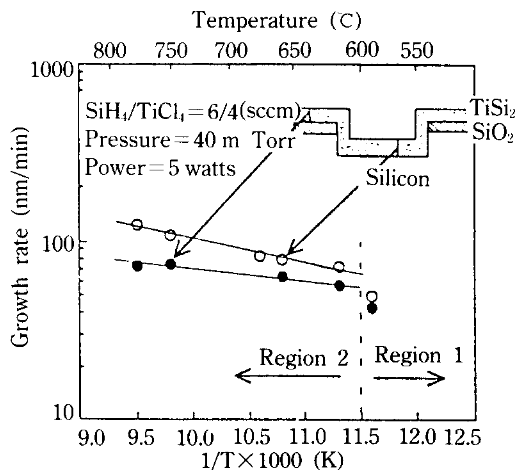


Fig 2. Arrhenius plot of the growth rate of $TiSi_2$ deposited on Si window and SiO_2 for 3 minutes.

rate on duration time and gas flow rate ratio was investigated at the constant temperature of 650℃ (region 2). According to CVD theory, region 2 can be defined as mass transport limited and region 1 as surface reaction limited.

At 570℃, no deposition of silicide occurred and several tiny etch pits were found scattered over the surface. As the temperature was increased to 590℃, the deposition started to take place. As the deposition temperature was increased above 600℃, the difference in the growth rates of silicide between on silicon and on SiO_2 increases. This indicates that, in the growth of silicide on silicon, increasing the temperature results in more silicon supplied from the substrate participating in the silicide formation.

Fig. 3 shows the thickness of the silicide deposited both on silicon and SiO_2 as a function of time. The error bars in the thickness of silicide are partly due to the surface roughness and partly due to the interface roughness. As shown in Fig. 3, the growth rate of silicide appears to be constant in time. This suggests that $TiSi_2$ growth is limited by the transport of gases ($TiCl_4$ and/or SiH_4) to the surface.

Fig. 4 shows the effects of silane gas flow rate on the thickness of silicide on silicon dioxide. As the SiH_4 flow rate increases, the thickness of the silicide increases and reaches a maximum value at a SiH_4 flow of 6 sccm, then it decrease. According to Fig. 2, the mass transfer of active radicals to the surface

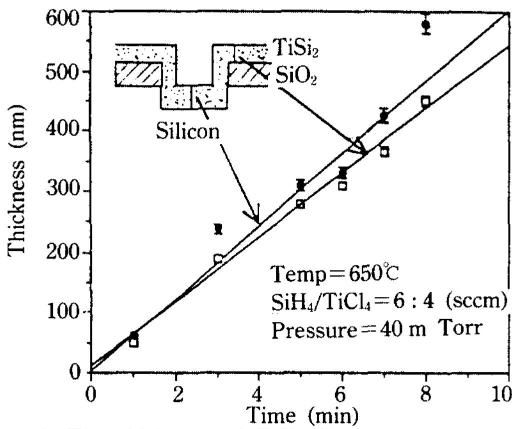


Fig 3. The thickness of $TiSi_2$ films deposited on Si window and on SiO_2, respectively, as a function of time.

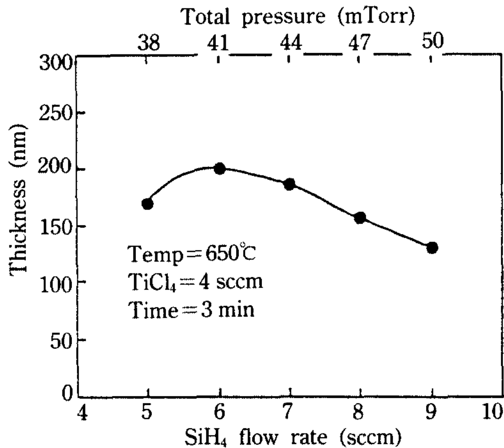


Fig 4. The thickness of $TiSi_2$ deposited on SiO_2 as a function of SiH_4 flow rate at 5 watts.

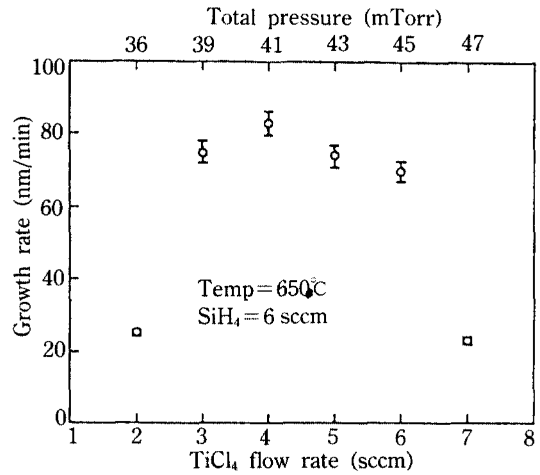


Fig 5. The average growth rate of silicide versus $TiCl_4$ flow rates for 3 minutes and 5 watts.

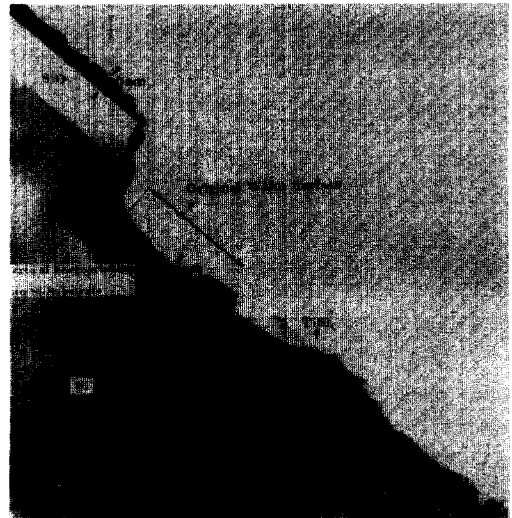
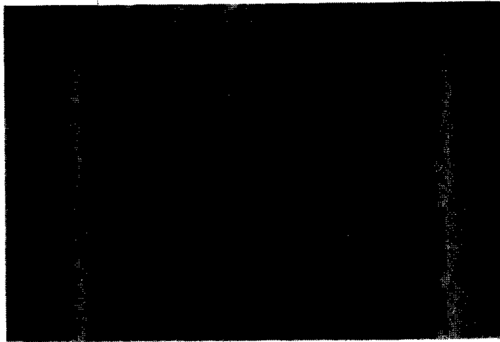


Fig 6. Cross-sectional TEM of $TiSi_2$ film with plasma cleaning prior to deposition of silicide at 650℃, at 6/4 (sccm), at 5 watts, and for 3 minutes.

limits the growth of the silicide at 650℃. Therefore, local equilibrium can be assumed to exist on the surface. Since silane radicals have high sticking coefficients, increasing silane gas flow rate increases concentration of adsorbed silane radicals on the surface and changes the ratio of adsorbed radicals. The change in the ratio of two reactants on the surface can influence the growth rate.

The effects of $TiCl_4$ gas flow rate on the growth rate are shown in Fig. 5. As the $TiCl_4$ gas flow increases, the growth rate also increases, reaches a maximum value, and then decreases. The decrease in the growth rate may be partly due to the reduced concentration of SiH_x radicals on the surface and partly due to the etching of the silicide which may occur with high chlorine concentrations. However, the evidence of etching of the silicide was not observed under SEM. The surface of silicide deposited on SiO_2 was usually smooth. Therefore, according to Figs. 4 and 5, both reactants ($TiCl_4$ and SiH_4) seemed to be limiting sources to silicide formation so that the maximum growth rate was obtained at the optimum gas ratios in the temperature range of region 2.



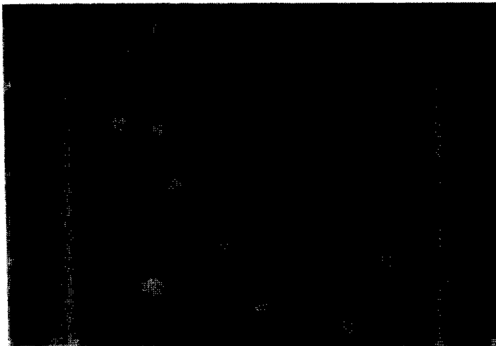


Fig. 7. SEM of $TiSi_2$ deposited on an oxide patterned wafer for 3 minutes, at 650℃, 5 watts and $SiH_4/TiCl_4$ flow ratio of 9a) 6/4, (b) 9/4 (sccm).

3.2. Silicon consumption

Fig. 6 shows the silicide deposited on a SiO_2 patterned wafer at 650℃, for 3 min, showing an uniform thickness on silicon as well as SiO_2. Excessive silicon consumption (3000~6000 A) was observed to result in the vertical encroachment into the silicon substrate, especially at the base of the contact cut. This vertical encroachment at the base of the contact window i.. Fig. 6 correponds to the rough surface at the edge of the silicon window shown in Fig. 7(a). In addition, the surface morphology of silicide on SiO_2 is smooth, while that of silicide on silicon is rough (see Fig. 7(b). These observations suggest that the surface roughness on silicon is not caused by the etching of the silicide, but by nonuniform silicon consmption as well as silicon etching. And the small difference (200~1000 A) in the thickness of silicide on silicon and on SiO_2 cannot be explained by the large amount of silicon consumed (3000~6000 A) if solid silicon is assumed to be a main contributor to silicide formation. Therefore, it is expected that a large fraction of silicon diffuses through the silicide layer and is etched away from the surface, while only a small fraction of silicon participates in silicide formation. Consequently, the silicon in the silane gas can be the main contributor to silicide formation. This fact is consistent with the constant growth rate in Fig. 3 and the observation of the maximum growth rate at the optimum gas ratios in Figs. 4 and 5.

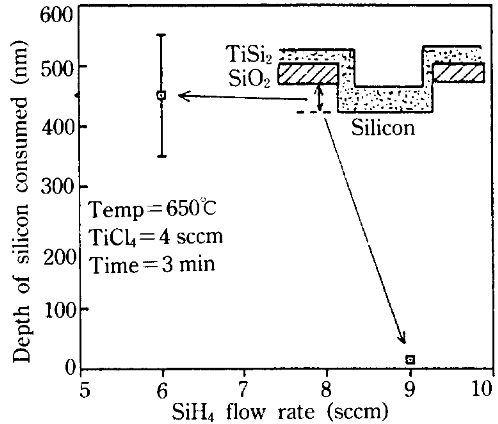


Fig. 8. The depth of silicon consumption versus SiH_4 flow rates for a constant $TiCl_4$ flow rate of 4 sccm, a deposition temperature of 650℃, and a power of 5 watts.

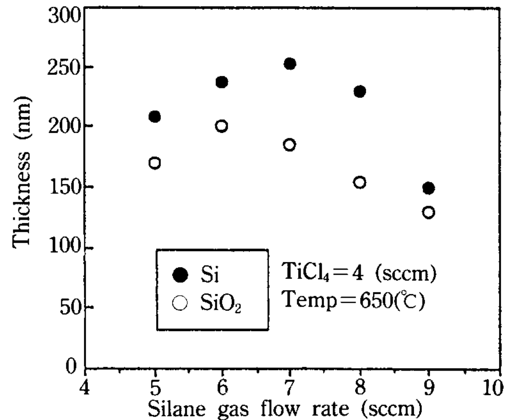


Fig. 9. The effects of SiH_4 flow rates on the difference of the thickness of $TiSi_2$ deposited on Si window and SiO_2.

Fig. 8 reveals an effect of SiH_4 flow rate on silicon consumption. The silicon consumption decreases rapidly at the SiH_4 flow of 9 sccm. Fig. 9 shows the influence of SiH_4 flow rates on the difference in the thickness of silicide on silicon and on SiO_2. The difference increases, reaches a peak, and then decreases rapidly when the gas flow rate is 9 sccm. The increase in the difference is attributable to more solid silicon participation in the silicide formation. The rapid decrease is due to a decrease in silicon consumption, as supported by Fig. 8. Therefore, silane seems to have two different effects on silicide formation depending on silane gas flow rates: 1) enhancing solid reaction with $TiCl_4$; 2) suppressing of silicon consumption.

3.3. Kinetic model of silicon consumption

A kinetic model is proposed to explain the effects of the SiH_4 gas flow rat on silicon consumption. Fig. 10 is a schematic representation of the process of silicon consumption as well as silane reaction. Silicon consumption can be modeled as a sequence of two events; first, silicon diffusion across a silicide layer and, second, surface reaction of solid silicon including silicide formation (displacement reation) and silicon etching. The flux of silicon across the silicide can be expressed as

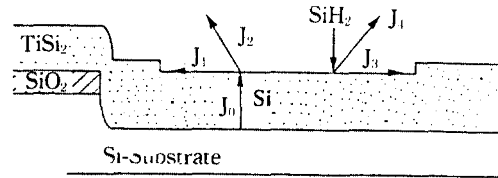
$$J_0 = D_0 \exp\left(\frac{-Q_0}{kT}\right) \frac{\partial[Si]}{\partial X}, \tag{1}$$

where J_0 is the diffusion flux of silicon across silicide layer, Q_0 is the activation energy for silicon diffusion, and [Si] is the concentration of silicon. The flux of surface reaction of solid silicon can be expressed in two paralled ways,

$$J_1 = K_1 \exp\left(\frac{-Q_1}{kT}\right) [Si]^5 [TiCl_2]^2 \tag{2}$$

$$J_2 = K_2 \exp\left(\frac{-Q_1}{kT}\right) [Si]^5 [TiCl_2] [H]^2, \tag{3}$$

where J_1 is the flux of silicon for silicide formation, J_2 is for silicon etching, Q_1 is the activation energy for silicide formation, Q_2 is for silicon etching and [ ] is the concentration of each species on the surface. We assume steady state condition during



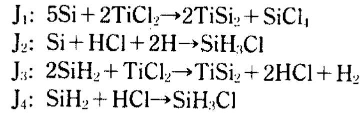


Fig. 10. Schematic representation of the process of silicon consumption and silane reaction.

silicon consumption, so the silicon flux can be expressed as

$$J_{Si} = J_0 = J_1 + J_2 \tag{4}$$

According to equation 4, the silicon consumption is limited by either silicon diffusion across the silicide (J_0) or surface reaction of solid silicon on the surface (J_1 and J_2). If the mass transport of silicon across silicide limits the silicon consumption, the silicon consumption is not dependent on gas composition. However, Fig. 8 reveals that increasing silane gas flow rate decreases the silicon consumption, which suggests that the silicon consumption is controlled not by the mass transport of silicon across the silicide layer, but by the surface reaction of silicon on the surface for silicide less than 3000 A.

The surface reaction of silicon on the surface is proposed here to consist of two parellel reactions (J_1 and J_2), which suggest that, besides Si(s), HCl, $TiCl_4$, and H are necessary for the surface reaction of silicon. Therefore, gas composition is expected to strongly influence the surface reaction of silicon.

Fig. 7 shows that as SiH_4 increases, the surface morphology dramatically improves. Increasing the silane gas flow rate seems to suppress the etching of silicon by decreasing the concentration of adsorbed HCl. Fig. 9 shows that the difference between the thickness of silicide on silicon window and that on SiO_2 increases and reaches a peak when the silane gas flow rate is 7 sccm. This suggests that silicon diffusion from the substrate is participating more in the formation of silicide when the silane gas flow rate is increased. Increasing silane gas flow rate enhances a surface reaction path of silicon to

silicide formation, while suppressing silicon etching, J_2, due to the consumption of HCl. Therefore, the gas composition may decide the surface reaction path of silicon either to silicide formation or to silicon etching with different activation energies by influencing the concentration of HCl. In addition to the dependence of SiH_4 flow rate on the surface reaction of silicon, the reaction of solid silicon with $TiCl_2$, at high SiH_4 flow rates, competes with the reaction of SiH_2 with $TiCl_2$. Fig. 8 reveals that the silicon consumption rate at 9 sccm of SiH_4 flow rate is much lower than that at 6 sccm. This suggests that increasing silane gas flow rate increases the forward reaction of J_3 while retarding the displacement reaction of silicon, thus leading to low consumption of silicon. From this consideration, it is evident that high silane flow rate effectively suppresses the silicon consumption.

3.4. Blanket silicide with no Si consumption

XTEM of a silicide deposited at 590℃ with a gas ratio ($SiH_4/TiCl_4$) of 8/4 (sccm) shows a conformal step coverage and no Si consumption from the substrate (see Fig. 11). This silicide film with no silicon consumption has promising applications to shallow junction contacts as well as *via* hole fillings.

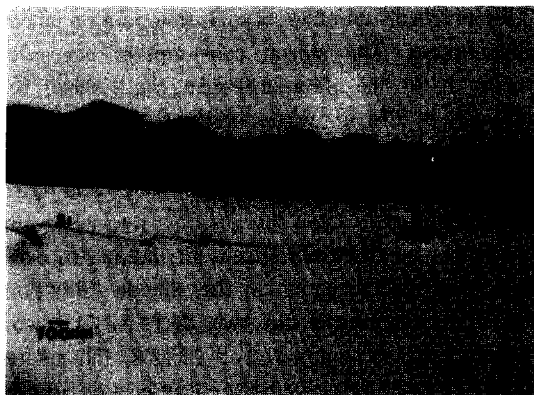


Fig. 11. Cross-sectional TEM of blanket titanium silicide deposited on an oxide patterned wafer for 5 minuets, at 590℃, $SiH_4/TiCl_4$ flow ratio of 8/4 (sccm), and 5 watts.

4. Summary

The effects of experimental parameters on the growth of silicide and its concomitant silicon substate consumption have been investigated. The deposition rate was divided into two distinct regions depending on the temperatue and the reaction was controlled by the mass transfer of reactants at 650℃. XTEM of the silicide deposited at 650℃ and $SiH_4/TiCl_4$ of 6/4 (sccm), revealed the small difference (200~1000 A) between the thickness of silicide on silicon and silicide on SiO_2 compared with the large amount of silicon consumption (3000~6000 A), suggesting that most of solid silicon consumed from the substrate was etched away from the surface. Consequently, silane seemed to be main contributor to silicide formation and solid silicon a minor contributor in the temperature of region 2.

The growth rate was strongly influenced by SiH_4 and $TiCl_4$ flow rates at 650℃. As SiH_4 was increased, the growth rate first increased and then decreased. A similar trend in growth rates was observed for $TiCl_4$. Both reactants seemed to be limiting sources to silicide formation so that the maximum growth rate was obtained at the optimum gas ratio.

Silicon consumption rapidly decreased from 4500 to less than 100 A when the silane gas flow rate increased from 6 to 9 sccm at the constant $TiCl_4$ flow rate of 4 sccm at 650℃. A conformal silicide with no silicon consumption was deposited at 590℃, and at 8/4 (sccm) of $SiH_4/TiCl_4$ flow ratio. Both results confirmed the strong effects of temperature and silane gas flow rate on silicon consumption.

The proposed kinetic model of silicon consumption provides a qualitative description of the effects of the silane gas flow rate on silicon consumption, indicating why low deposition temperature as well as the high silicon flow rate is effective in suppressing silicon consumption.

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