Plasma Enhanced Chemical Vapor Deposition of Blanket $TiSi_2$ on Oxide Patterned Wafers

II. Silicide Properties

Jaegab Lee and Rafael Reif

Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

ABSTRACT

A cold-wall plasma enhanced chemical vapor deposition (PECVD) system has been used to investigate the effects of deposition variables on the properties of titanium disilicide deposited on oxide patterned wafers. The as-deposited films have low resistivities in the range of 14 to 25 μΩ cm as a function of temperature and $SiH_4/TiCl_4$ flow rate ratios, and show the preferred orientation of the C-54 $TiSi_2$ phase. The surface of the silicide film on SiO_2 is smooth, while that of the film on silicon is rough. The surface roughness of the silicide on silicon is affected mainly by gas flow rate ratios. Cross-section transmission electron microscopy of the films annealed at 950°C for 30 min in a nitrogen ambient shows the stable silicide underneath an amorphous layer. This suggests that as-deposited silicide films on SiO_2 can withstand a high temperature process, and have good adhesion on SiO_2. Finally, as an application of this PECVD $TiSi_2$ as gate electrode material, the polycide structure was realized. The low resistivity (17 to 19 μΩ cm) silicide film deposited on polysilicon reveals a good interface between silicide and polysilicon, and a smooth surface.

Titanium disilicide has been used as gate, contact, and interconnect metallization in integrated circuit technologies due to its low resistivity and the low annealing temperature required to form the stable silicide phase. However, as the thrust of ULSI continues, silicides used as gates, interconnects, and contacts must satisfy more restricted requirements. The use of silicide as a contact to shallow junctions on Si integrated circuits requires limited silicon substrate consumption and a smooth interface between the silicide and the silicon substrate. A rough interface leads to junction leakage (1). Silicide used as an interconnect or gate electrode needs good adhesion to silicon dioxide and good thermal stability so that it can withstand high temperature processes. Recently, refractory metals and silicides have been directly deposited on gate dielectrics instead of on polysilicon to improve the turn-off characteristics of p-channel metal oxide semiconductor field effect transistors (MOSFET) (2). Consequently, process issues such as thermal stability and adhesion to gate oxide must be satisfied before this technology can be applied to complementary metal oxide semiconductor (CMOS) integrated circuits (ICs).

There are a number of articles discussing the temperature stability of $TiSi_2$ at temperatures greater than 850°C (3-9). The work reported by researchers concludes that high temperature annealing of $TiSi_2$ on doped or undoped polysilicon, or on single crystalline silicon, is unstable due to titanium silicide agglomeration (4-6) and/or epitaxial growth of silicon in the silicide film through the transport of Si atoms into the deformed titanium silicide (7-9). However, until now, the high temperature stability of $TiSi_2$ on SiO_2 has not been discussed. This is important, as it will permit study of the role of the presence of poly or single crystalline silicon on silicide degradation.

In this paper, we will explore the effects of deposition variables on the material properties of PECVD titanium disilicide films on silicon and silicon dioxide, including surface morphology, resistivity, structure, and composition. In addition, as-deposited films annealed at 950°C in a nitrogen ambient will be used to investigate the thermal stability and adhesion of titanium silicide on silicon dioxide. Finally, a polycide structure will be realized and used for the study of the material properties of silicide on polysilicon.

Deposition Process

We have developed a high vacuum system for PECVD of stable titanium silicide films on oxide patterned wafers. The details of the reactor are described in Part I (10). Depositions have been carried out on 4 in., n-type silicon wafers under the conditions summarized in Table I. A typical plasma titanium silicide deposition consists of an *in situ* hydrogen plasma cleaning followed by a silicide deposition.

For the polycide structure, a sequential deposition of polycrystalline silicon and titanium silicide is carried out after *in situ* hydrogen plasma cleaning. The polysilicon was deposited at 650°C, with a SiH_4 flow rate of 6 sccm, the total pressure of 30 mTorr, and the duration time of 30 min.

Results and Discussion

Resistivity.—As-deposited films consist of the stable $TiSi_2$ phase, so postannealing is not required to reduce the resistivities of silicide films. As shown in Fig. 1, the resistivities of the PECVD $TiSi_2$ films range from 14 to 25 μΩ cm depending on the SiH_4 flow rate at a constant $TiCl_4$ flow rate.

Structure and composition.—The typical x-ray diffraction peaks of as-deposited films on silicon show the preferred orientation of the C-54 $TiSi_2$ phase (Fig. 2(a)), which is compared with that of an as-deposited film on polysilicon consisting of the randomly oriented grains (Fig. 2(b)). The microstructure of films deposited by PECVD is composed of columnar structures.

X-ray diffraction patterns of $TiSi_2$ films as a function of temperature are shown in Fig. 3. Temperatures above 600°C enhance the preferred orientation, perhaps due to the enhanced mobility of the adsorbed species. The mobility of the adsorbed species is apparently large enough to inhibit renucleation on at least some crystal plane. Figure 4 shows the effects of gas flow ratio on the preferred orientation of $TiSi_2$ film. The higher flow rate of silane gas also enhances the degree of the preferred orientation. The silane gas seems to act as a driving force for the preferred orientation.

Rutherford backscattering spectroscopy (RBS) and Auger electron spectroscopy (AES) with depth profiling have been used to determine the Si/Ti ratio and impurities in the films. No impurities, such as carbon, oxygen, and chlorine, were observed in these films within the Auger de-

Table I. Deposition conditions

	H_2 Plasma	Titanium silicide
Temperature (°C)	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 (W)	15	5

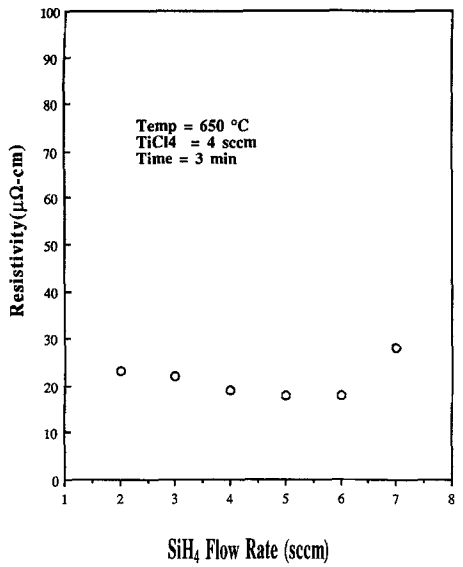


Fig. 1. The resistivities of titanium silicide *vs.* SiH_4 flow rates for a constant $TiCl_4$ flow rate of 4 sccm, a temperature of 650°C, and a power of 5 W.

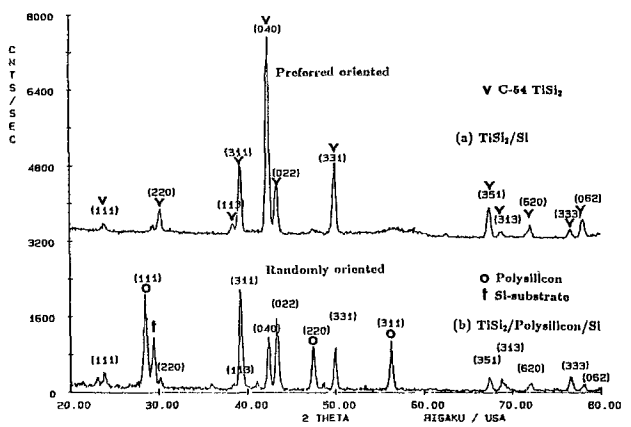


Fig. 2. X-ray diffraction pattern of $TiSi_2$ deposited on (a) silicon and (b) polysilicon for 650°C, 3 min, and 5 W deposition condition.

tection limit (1%). Figure 5 displays a plot of the Si/Ti ratio of as-deposited films determined by RBS as a function of $TiCl_4$ gas flow rate during deposition. The film composition has a stoichiometry of 2.04 to 2.07, showing its independence of the gas flow ratio.

Surface morphology.—Figure 6 shows the gas flow ratio effects on surface smoothness. As silane gas flow rate increases from 5 to 8 sccm, surface smoothness is dramatically improved. However, with flow rates higher than 9 sccm, whiskers start to appear. Increasing the silane gas flow rate improves the surface roughness by retarding the etching of silicon on the surface, as discussed in Part I (10).

The effects of dilute gases on surface morphology is shown in Fig. 7. As H_2 flow rate increases to 15 sccm, surface smoothness is improved, but sharp etch pits are observed. The etch pits may be due to the increased HCl and atomic hydrogen with increasing H_2. Increasing Ar flow rates also improves surface smoothness; however, significant whiskers are observed at 15 sccm. The addition of argon gas tends to favor filament growth. The addition of both diluents such as H_2 and Ar improves surface smoothness, but seems to influence the reaction paths in different ways.

Figure 8 shows the temperature dependence on the surface morphology. Tiny voids are observed on the surface of the silicide film deposited at 590°C. As the temperature is increased, the voids on the surface disappear. The void formations are probably due to lack of mobility of adsorbed species.

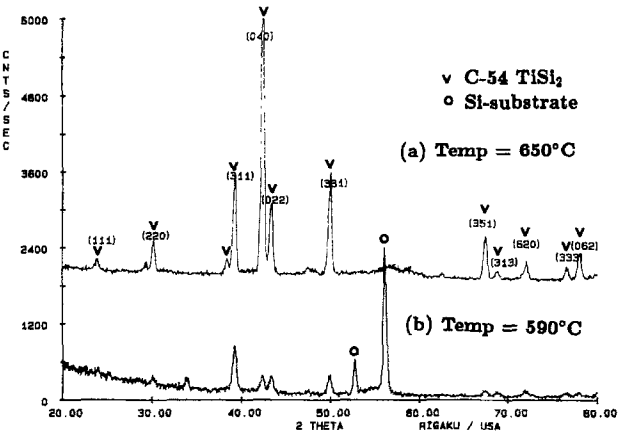


Fig. 3. X-ray diffraction pattern of $TiSi_2$ deposited at (a) 650° and (b) 590°C for a $SiH_4/TiCl_4$ flow rate ratio of 6/4, 5 W deposition condition.

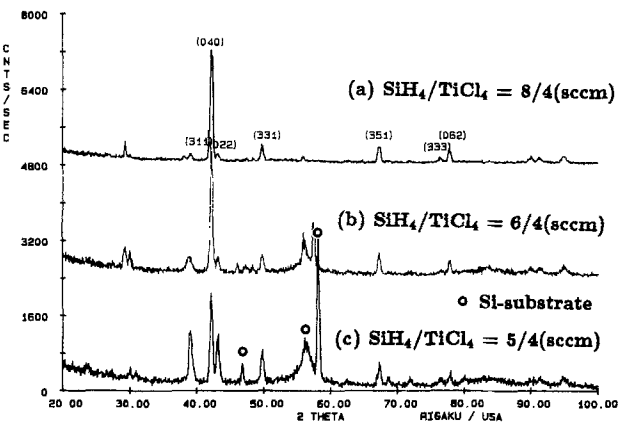


Fig. 4. X-ray diffraction pattern of $TiSi_2$ deposited on 650°C, 5 W showing the effects of SiH_4 flow rates on the preferred orientation.

Thermal stability.—The thermal stability of $TiSi_2$ deposited on silicon dioxide was examined by annealing the sample at 950°C for 30 min in a nitrogen ambient (see Fig. 9(a)). The TEM cross section of the annealed sample shown in the Fig. 9(b) reveals the stable titanium silicide underneath an amorphous layer of about 800 Å. The amorphous layer consists of oxygen, silicon, and titanium as detected by RBS and shown in Fig. 10, which indicates that

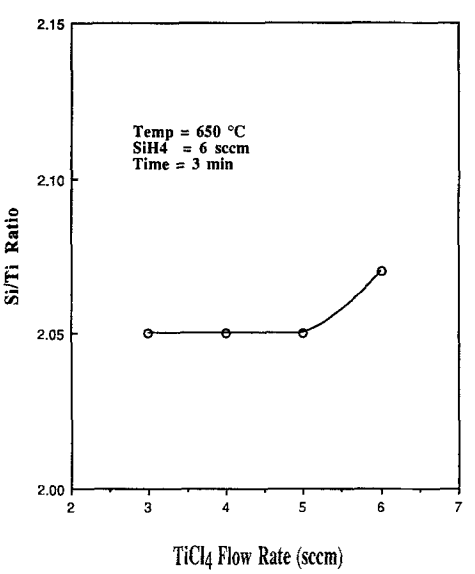


Fig. 5. The Si/Ti ratio of titanium silicide films *vs.* $TiCl_4$ flow rates determined by RBS for a constant SiH_4 flow rate of 6 sccm, 650°C, 3 min, and 5 W deposition condition.

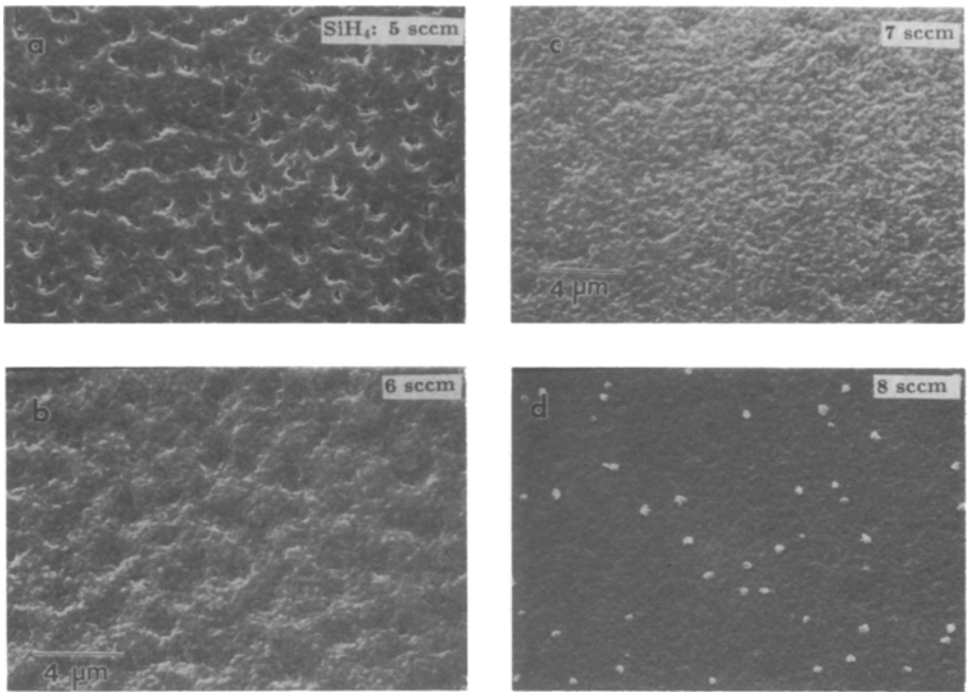


Fig. 6. SEM of $TiSi_2$ films deposited at a SiH_4 flow rate of (a) 5, (b) 6, (c) 7, and (d) 8 sccm for a constant $TiCl_4$ flow rate of 4 sccm, 650°C, 3 min, and 5 W deposition condition,

the top of silicide was incompletely oxidized. The sheet resistance of the film changed from 1.1 to 1.6 Ω/□, which is attributed to the decrease in the active thickness of silicide underneath the amorphous layer. SEM showed no morphological changes in the films. Annealing at 950°C for 30 min also did not change the appearance of $TiSi_2$ x-ray peaks. These results indicate that as-deposited PECVD titanium silicide on silicon dioxide can withstand a high temperature process and has good adhesion to SiO_2.

Comparison of this result with previous observations reported by other authors suggests that the temperature instability of silicide on polysilicon or single crystal silicon is enhanced by the presence of silicon. In other words, thermodynamical surface energy reduction is a driving force for silicide degradation, which is enhanced kinetically by providing the path for silicon diffusion within silicide.

This result also suggests potential applications of $TiSi_2$ as a gate electrode directly because little interaction was observed between the silicide and silicon dioxide, as shown in Fig. 9. Moreover, $TiSi_2$ offers a work function near the middle of the silicon bandgap, resulting in a nearly identical work function difference for both an n- and p-type substrate. Therefore, with the material properties advantage of $TiSi_2$, such as good adhesion to SiO_2, high temperature stability, little interaction of silicide with SiO_2, and a proper work function value, $TiSi_2$ is a good candidate for CMOS gate electrode.

Polycide structure.—A polycide structure was realized by the sequential deposition of LPCVD polysilicon and PECVD titanium silicide. After deposition of polysilicon, the titanium silicide was deposited under the conditions of temperature at 650°C, a $SiH_4/TiCl_4$ flow ratio of 6/5 (sccm), a power of 5 W, and a duration time of 3 min. The TEM cross section of the silicide film shows a smooth interface between titanium disilicide and polysilicon, as shown in Fig. 11. Figure 11 also reveals the surface smoothness of silicide corresponding to the surface roughness of polysili-

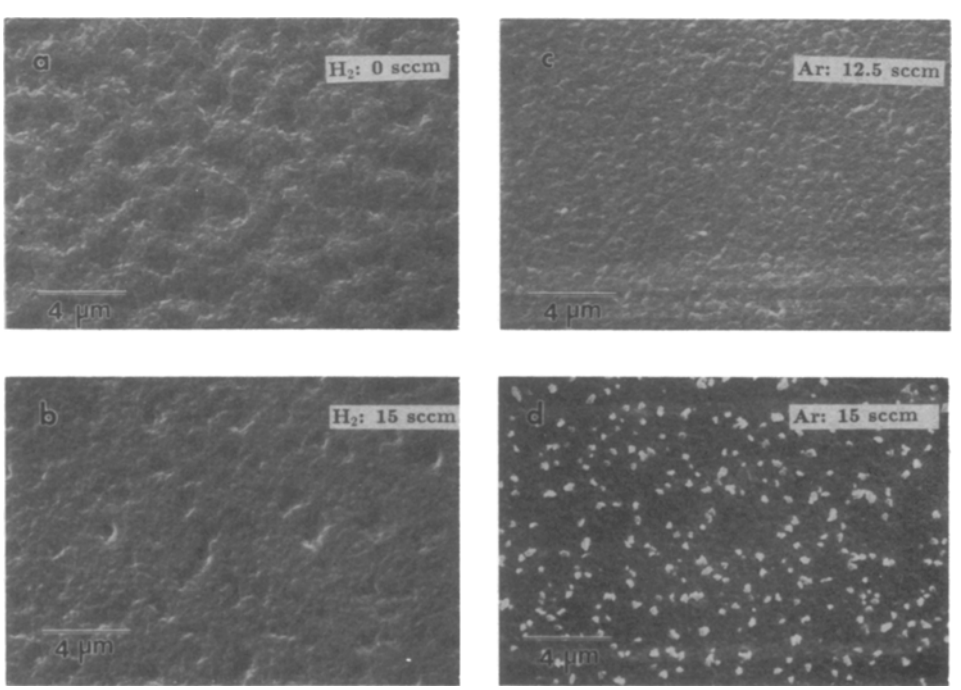


Fig. 7. SEM of $TiSi_2$ deposited at H_2 flow rate of (a) 0, (b) 15 sccm, and at Ar flow rate of (c) 12.5 , (d) 15 sccm for a constant $SiH_4/TiCl_4$ flow rate ratio of 6/4, 650°C, 3 min, 5 W deposition condition.

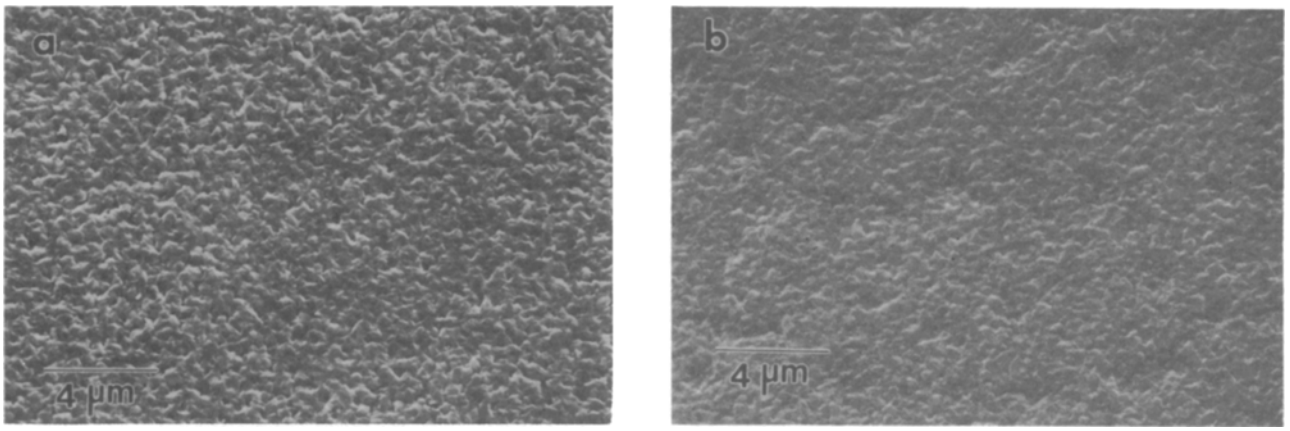
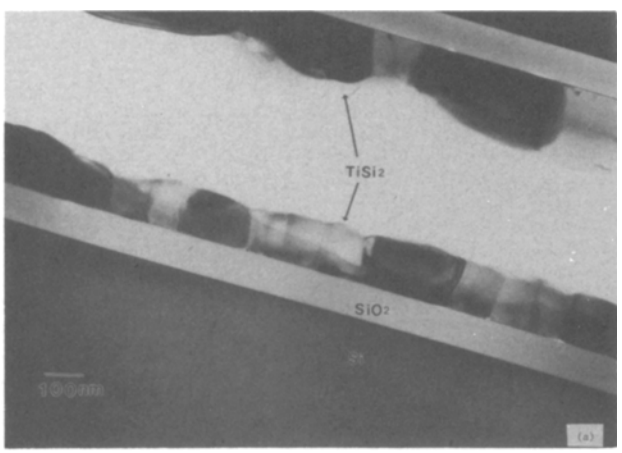


Fig. 8. SEM of $TiSi_2$ deposited at a temperature of (a) 590° and (b) 650°C for a constant $SiH_4/TiCl_4$ flow rate ratio of 6/4, 40 mTorr, 3 min, 5 W deposition condition.



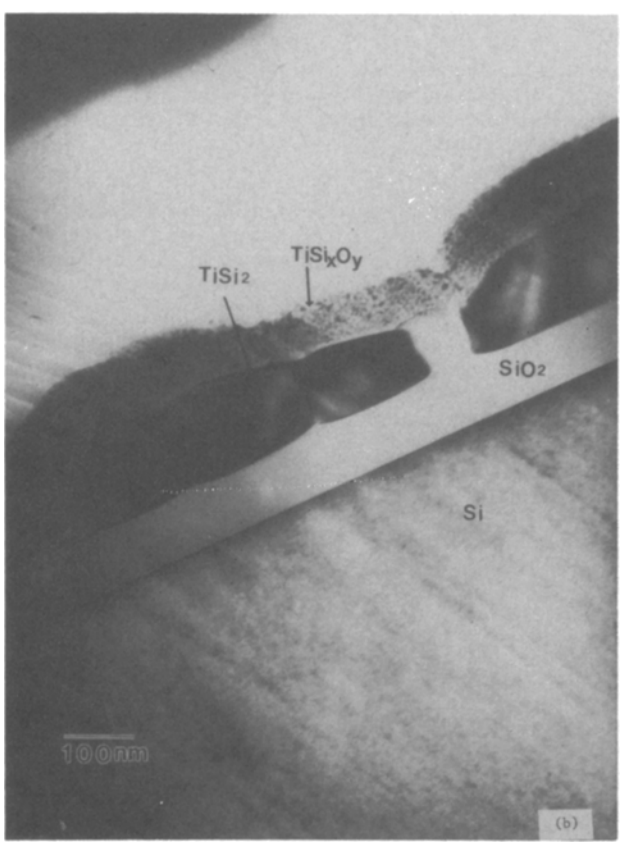


Fig. 9. Cross-sectional TEM of (a) as-deposited $TiSi_2$ on SiO_2 at 650°C and $SiH_4/TiCl_4$ flow ratio of 6/4, (b) $TiSi_2$ film annealed at 950°C, in N_2 ambient, for 30 min.

con. The silicide thickness (2000 to 2400 Å) on polysilicon is similar to that of silicide (2100 to 2250 Å) deposited under the same conditions on silicon in an oxide patterned wafer. The film deposited on polysilicon has the random orientation of C54 $TiSi_2$ phase, shown in Fig. 2, and a low resistivity of 17 to 19 μΩ-cm. Therefore, PECVD $TiSi_2$ can be applied for a polycide structure as well as for a contact structure simultaneously.

Summary

The use of plasma in this system allows considerable versatility, from hydrogen plasma etching prior to deposition, to the activation of the gas reaction at low temperatures, which enables the deposition of C-54 $TiSi_2$ films at 590°C.

The properties of $TiSi_2$ films deposited by PECVD have been investigated against temperatures, $SiH_4/TiCl_4$ flow

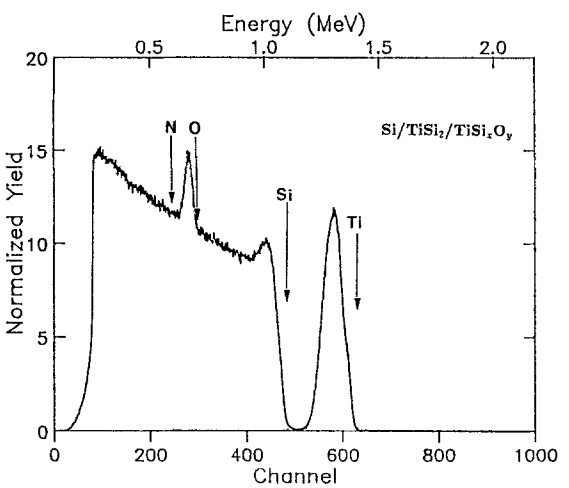


Fig. 10. RBS spectra of $TiSi_2$ film annealed at 950°C, in N_2 ambient, for 30 min.

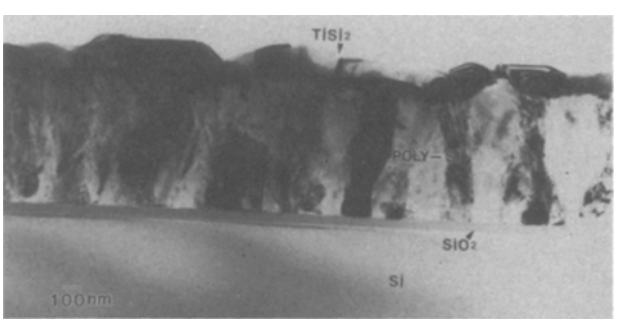


Fig. 11. Cross-sectional TEM of $TiSi_2$ deposited on polysilicon for a $SiH_4/TiCl_4$ flow rate ratio of 6/5, 3 min, 5 W deposition condition.

rate ratios, and dilution gases (H_2, argon). The as-deposited films show low resistivities (14 to 25 μΩ-cm) as a function of gas flow rate ratios, and reveal the preferred orientation of the C-54 $TiSi_2$ phase. The degree of the preferred orientation was enhanced with increased silane gas flow rate and temperature.

The surface morphology of the silicide films deposited on silicon dioxide is usually very smooth, while that on silicon windows is rough and is influenced largely by the gas flow rate ratios. This is attributed to the fact that silicon is diffused to the surface through the titanium silicide and is then etched away, leading to the recess of silicide into the silicon substrate. Higher silane gas flow rates improved the surface morphology dramatically by retarding silicon etching.

The cross-sectional TEM of a silicide film annealed at 950°C, for 30 min in a nitrogen ambient showed the stable silicide underneath an oxidized amorphous layer. The sheet resistance of the film changed from 1.1 to 1.6 Ω/□ on annealing at 950°C. The x-ray peaks of the annealed sample did not change upon annealing. This suggests that the as-deposited silicide film can withstand high temperature processes with good adhesion to silicon dioxide.

This reactor system was also used to deposit *in situ* a polycide structure consisting of polysilicon followed by the $TiSi_2$ layer. The as-deposited titanium disilicide on polysilicon showed a smooth interface and a smooth surface corresponding to the surface roughness of polysilicon.

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Wet Silicon Etching with Aqueous Amine Gallates

H. Linde and L. Austin

IBM General Technology Division, Essex Junction, Vermont 05452

ABSTRACT

A safe, aggressive formulation is described for wet anisotropic etching of single-crystal silicon. This etchant contains ethanolamine, gallic acid, water, pyrazine, peroxide, and a surfactant, and achieves etch rates of up to 140 μm/h on (100) Si, stopping on high boron concentrations (>3E19 atoms/cm²). The etchant addresses safety and disposal concerns, and supersedes ethylenediamine formulations for the fabrication of silicon structures.

Anisotropic etching of single crystal silicon has been used to fabricate monolithic integrated circuits, trenches, channels, membranes, and diffraction gratings for optical devices (1-5). Etching for such three-dimensional microstructures has been well reviewed by Kern (6) and Bassous (7), where (100) anisotropy is attributed to the density of surface-free bonds, which are a consequence of crystallographic structure (7). The etch geometry is shown in Fig. 1.

Etchants for this process are generally aqueous alkaline solutions based on sodium (8, 9) or potassium hydroxide (10-12), hydrazine (13, 14), quaternary ammonium hydroxides (15), sodium silicate (9), or ethylenediamine (13, 16-18). These etchants interact through oxidation of the surface with water (liberating hydrogen), and dissolution of the oxidized product. Alcohols such as propanol (19, 20), isopropanol (12, 14), or butanol (19) slow surface attack of hydroxide, while catechol (16-18) in ethylenediamine produces a silicon complex that aids dissolution.

The essential feature for anisotropy is that the reaction rate in the (100) Si plane is 50 to 100 times faster than in the (111) plane, producing V-shaped sidewalls 54 degrees from the (100) surface. Anisotropic etchants have further been shown to generally slow down or stop at high boron concentrations (3E19 atoms/cm²) (17-18), making it possible to produce thin boron-rich structures on the surface of thick silicon substrates.

Hazards

Although ethylenediamine-catechol etchants have been commonly used to fabricate microstructures, they have been judged unduly hazardous. Ethylenediamine is reported to cause allergic respiratory sensitization, and catechol is described as a toxic corrosive. The use of these etchants in laboratory or manufacturing processes creates undue risk during use and on disposal.

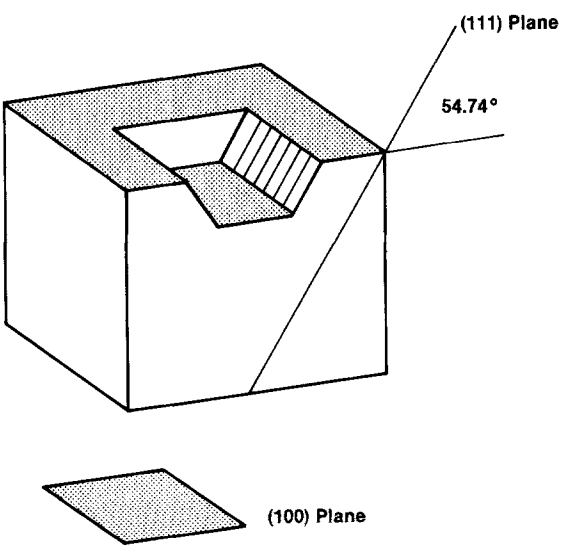

Fig. 1. Anisotropic etch geometry.