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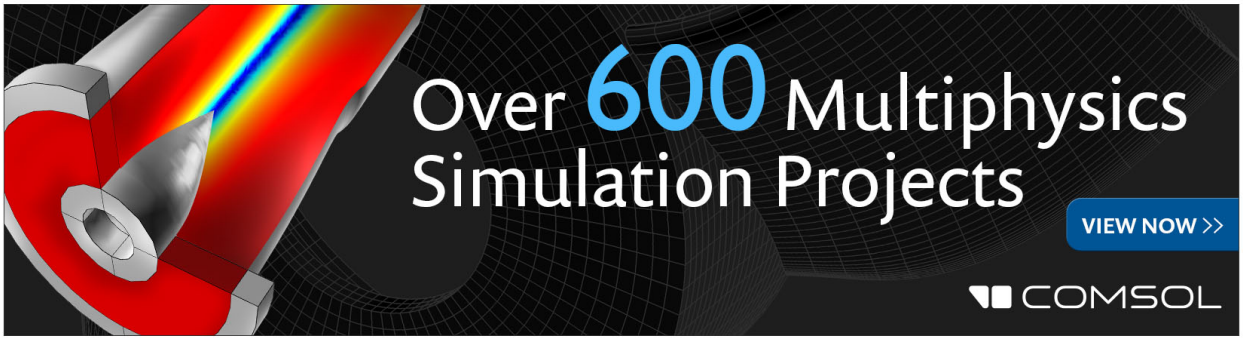

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Highly selective sputtering of silicon from $TiSi_2$ at elevated temperature

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We demonstrate almost 100% selective sputtering of silicon from $TiSi_2$ using a combination of low energy ion bombardment and elevated temperature. $TiSi_2$ was prepared by annealing 1000-Å-thick Ti on (100)Si in He at 635 °C for 30 min to produce 2300-Å thick $TiSi_2$. Ion beam etching was carried out using 300 eV argon with a flux of 0.27 mA/cm^2 at temperatures from 33 to 700 °C. *In situ* sheet resistance measurements were used to monitor the decrease in silicide thickness as a function of time. Near room temperature, ion etching causes normal sputtering of the silicide. However, at temperatures of 500–700 °C, the sheet resistance remains almost unchanged during ion beam etching. Analysis by Rutherford backscattering, with and without Xe markers, shows that Si atoms sputtered from the surface of these high-temperature samples are continuously replaced by Si diffusing from beneath the silicide layer. The thickness and composition of the silicide remain almost unchanged, but the dramatic change in sputtering behavior shows that the surface is enriched in Si. Compared with the room-temperature values, the absolute sputtering yield of Ti at 500–700 °C is decreased by a factor of 5, and the yield of Si is increased by a factor of 2. The net result is almost 100% selective sputtering of silicon.

The sputtering yield of a single-element material is approximately independent of temperature up to the melting point.[1] Also, for alloys and compounds, the sputtering yields do not strongly depend on temperature unless diffusion occurs during ion bombardment. The diffusion of one constituent towards the surface has been shown to cause preferential sputtering in alloys of Ni-Ag[2] and Cu-Ni,[3] and in compounds PtSi, $MoSi_2$, and NiSi.[4] In these cases, diffusion during ion etching establishes composition gradients up to several micrometers deep, determined by the temperature and preferential sputtering yields. Bilayers of Ni/Ni_3C have also been shown to develop highly preferential sputtering.[5] In this letter, we describe a related effect in the sputtering of $TiSi_2$ at elevated temperature, in which highly selective sputtering of Si develops in a thin layer of $TiSi_2$ on bulk Si. Near room temperature, normal sputtering of both Ti and Si atoms occurs, causing removal of the silicide layer. At temperatures of 500–700 °C, however, we show that Si atoms removed by sputtering are replaced in a steady-state process by Si diffusing to the surface from beneath the silicide layer. Since the supply of Si atoms is not depleted, almost 100% selective sputtering of Si is achieved.

$TiSi_2$ was formed by evaporating 1000 Å Ti onto BHF-cleaned undoped (100)Si and annealing in He at 635 °C for 30 min. This treatment gives a thickness of 2300 Å $TiSi_2$ with a resistivity of 45–65 $\mu\Omega$ cm. X-ray diffraction shows the film to be primarily C49 $TiSi_2$, with a small fraction of C54 phase.[6] Ion bombardment was provided by a Kaufman source operating in 2×10^{-4} Torr (2.7×10^{-2} Pa) Ar at an ion energy of 300 eV and flux of 0.27 mA/cm^2. The system base pressure was typically 1.0×10^{-7} Torr (1.3×10^{-5} Pa). Samples were mounted on a resistively heated Mo holder, with a chromel-alumel thermocouple touching the sample. The temperature was stabilized at 33–700 °C during ion bombardment for times up to 25 min. During ion etching, the sheet resistance was monitored by four tungsten probes. The etched step heights were measured by a profilometer, and the composition, structure and thickness of the $TiSi_2$ layer were determined by Rutherford backscattering (RBS) and x-ray diffraction. The identity of the dominant moving species was established by Xe marker experiments.

The dependence of sheet conductance on ion etching time is shown in Fig. 1 for sample temperatures of 33–700 °C. The values are normalized to the sheet conductance prior to ion etching. At the two highest temperatures (600 and 700 °C), the resistance of the Si substrate became too low for accurate measurements of the silicide resistance. For these measurements, room-temperature sheet resistance readings were taken between sequential exposures to ion etching at high temperature. After an initial decrease due to sample heating, the linear decrease in conductance for the 33 °C sample reflects the linear decrease in silicide thickness caused by a steady sputtering rate. The silicide is completely sputtered away after 25 min as shown by the lowest curve in Fig. 1. As the temperature is increased to 500–700 °C, the sheet resistance becomes almost independent of etching time, indicating that the silicide thickness is not being reduced by sputter etching. RBS analysis was made on samples from Fig. 1 etched for 5, 10, and 15 min, the latter shown in Fig. 2. These spectra confirm loss of silicide thickness in the lower temperature samples (33 and 400 °C) and decreased loss in the 500 °C sample. The silicide thickness remains almost unchanged in the higher temperature samples (600 and 700 °C). X-ray diffraction indicates a slight increase in the fraction of C54 $TiSi_2$ in the 600 and 700 °C samples, as expected from the onset of thermal transformation to the lower resistivity phase.[6–8] Some contamination of the $TiSi_2$ surface by up to several monolayers W (Fig. 2) came from sputtering of the W probes, but was not found to affect the etching process.

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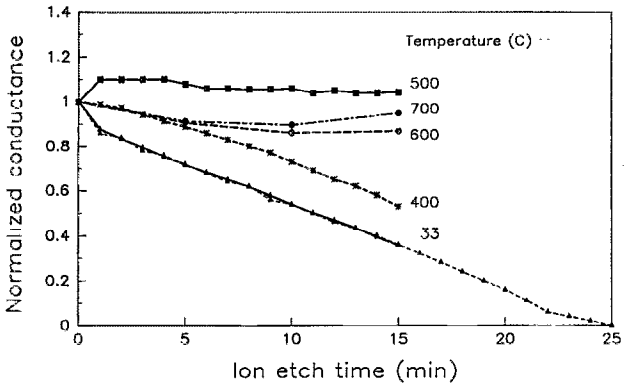

FIG. 1. Normalized sheet conductance vs time for 2300 Å thick $TiSi_2$ on Si, during Ar^+ ion beam etching (300 eV, 0.27 mA/cm^2) at temperatures of 33–700 °C.

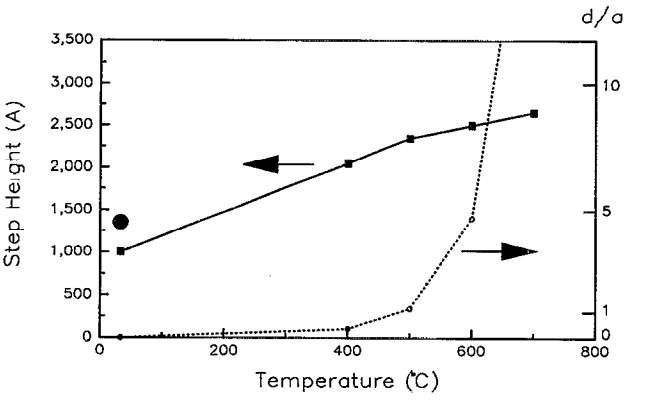

FIG. 3. Step heights of ion etched surfaces of $TiSi_2$ after 15 min ion beam etching, as a function of temperature from 33 to 700 °C. The height determined from RBS measurement at 33 °C is shown as an added data point. The dotted curve shows the ratio of diffusion length to sputtered thickness in 1 s for Si diffusing through $TiSi_2$.

To verify that ion etching actually occurred in the higher temperature samples, step height measurements (Fig. 3, solid line) were made relative to adjacent masked areas. The step height obtained at 33 °C after 15 min ion etching is 1000 Å, corresponding to an etch rate of 67 Å/min. The RBS and sheet conductance results indicated a higher etch rate of 90–100 Å/min. Since the step height measurement indicated some surface roughness, the higher value of 90 Å/min will be used for comparison. At higher temperatures, the step height increased to 2500 Å, corresponding to an etch rate of 167 Å/min.

Summarizing these results, ion etching at 33 °C produces the expected loss of thickness of the $TiSi_2$ layer by sputtering of both Ti and Si atoms. At temperatures of 500–700 °C, however, the silicide thickness remains almost constant during ion etching. The thickness of material actually removed is increased to twice the value at 33 °C (Fig. 3). Since the Ti RBS peak area remains almost unchanged in the high-temperature samples, it is clear that the removed material is almost entirely Si. Two mechanisms could account for this behavior. Either Ti atoms are diffusing away from the surface towards the underlying Si, or Si atoms are diffusing towards the surface and replacing sputtered Si atoms. During ion etching, the surface is receding about $a = 3$ Å in one second. From Raaijmakers,[9] we estimate lower limits for the Si diffusion length d in one second to be 1 Å at 400 °C, 3.4 Å at 500 °C, 14 Å at 600 °C, and over 60 Å at 700 °C. The ratio d/a, shown in Fig. 3 as a dotted line, rises sharply in the temperature range of 400–600 °C, indicating that Si diffusion dominates over sputter removal at high temperature.

To confirm that Si is the dominant moving species, samples of the same $TiSi_2$ thickness were implanted with 2×10^{15} Xe^{++} ions/cm^2 at 180 keV with a projected range of 1000 Å to provide a marker within the silicide. These samples were ion etched at temperatures of 33, 400, 500, 600, and 700 °C for times of 5, 10, and 15 min each. Argon ion bombardment at 33 °C for 15 min caused sputter etching of the $TiSi_2$ layer and partial removal of the Xe marker by sputtering. However, the remaining Xe did not move relative to the underlying $TiSi_2$/Si interface. At

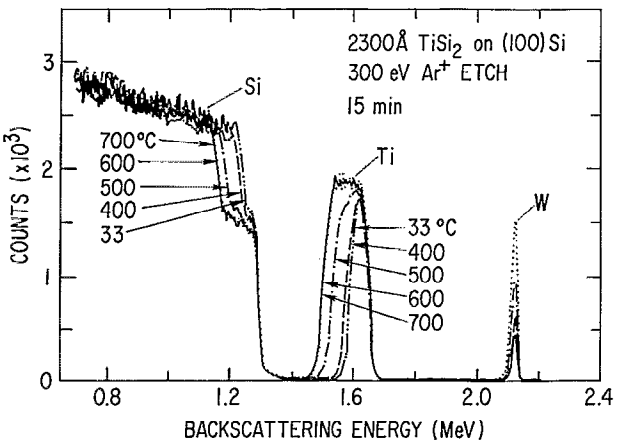

FIG. 2. Rutherford backscattering spectra of $TiSi_2$ films on Si (shown in Fig. 1) after 15 min Ar^+ ion beam etching at temperatures of 33–700 °C. The spectra of nonetched samples and those etched at 600 and 700 °C are indistinguishable.

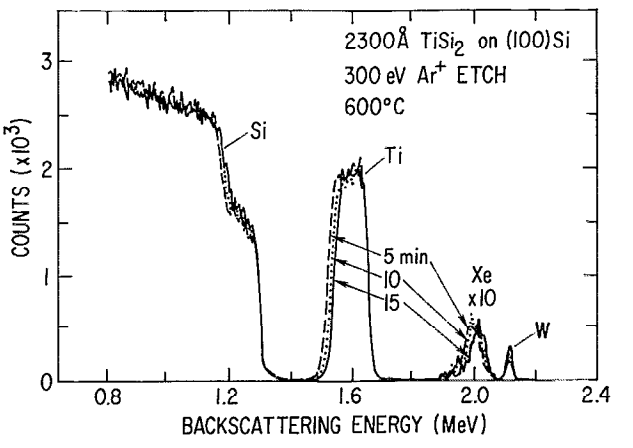

FIG. 4. Rutherford backscattering spectra of Xe-implanted $TiSi_2$ on Si after ion beam etching for 5, 10, and 15 min at 600 °C. The region showing the Xe marker is magnified by 10.

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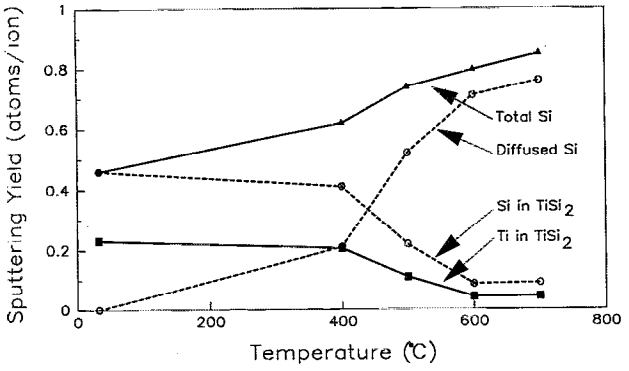

FIG. 5. Absolute sputtering yields of Ti and Si vs temperature for 300 eV Ar^+ ion bombardment of 2300-Å thick $TiSi_2$ layer on Si. The Ti yield is from Ti sputtered from $TiSi_2$. The Si yield shown as the component sputtered from $TiSi_2$, the component supplied by diffusion, and the total Si yield.

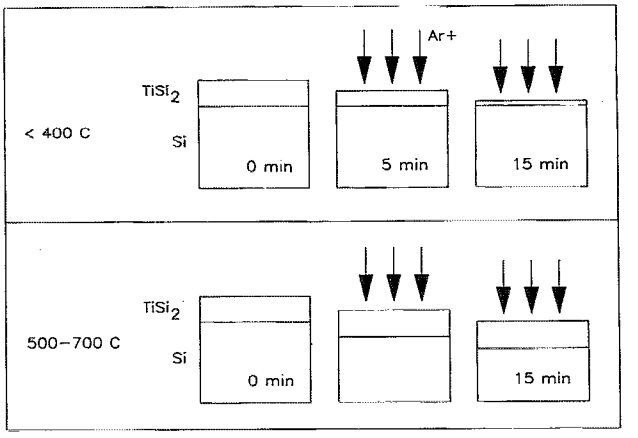

FIG. 6. Schematic diagram indicating sputtering of $TiSi_2$ layer on Si at low temperature (<400 °C) and at high temperature (500–700 °C). At high temperature, the $TiSi_2$ layer thickness remains almost unchanged.

600 °C, argon ion etching caused far less thinning of $TiSi_2$. The spectra measured after 5, 10, and 15 min etching (Fig. 4) show that the Xe marker is intact, and remains fixed relative to the $TiSi_2$/Si interface remained unchanged. This confirms that Si atoms diffuse to the surface from beneath the silicide layer during elevated temperature ion etching.

The values of sputtering yield change dramatically with increasing temperature (Fig. 5). We discuss only the absolute sputtering yield, equal to the number of atoms removed per incident ion. Four curves are shown in Fig. 5, namely the Ti yield determined from RBS, the yield of Si in $TiSi_2$ (twice the Ti yield), the yield of Si diffused from below the silicide, and the total Si yield. Near room temperature (33 °C), the sputtering yields are 0.23 Ti atoms/ion and 0.46 Si atoms/ion. For comparison, the single element yields are 0.35 atoms/ion for both pure Si and Ti.[10] At high temperature (600–700 °C), the Ti yield decreases to 0.04 Ti atoms/ion, while the Si yield increases to 0.85 Si atoms/ion. In this range, 95% of the sputtered flux is composed of Si atoms. Sublimation of Si or SiO is insignificant at these temperatures, since their vapor pressures are below 10^{-8} Torr (1.3×10^{-6} Pa).

The high values of Si sputtering yield and near absence of Ti sputtering at high temperature indicate that the surface is enriched with Si, consistent with measurements of Si segregation.[11] If the surface is covered with at least one monolayer of Si atoms, we expect almost 100% selective sputtering of Si by 300 eV Ar^+ ions, for which sputtered atoms originate primarily in the top monolayer.[12] Also, the sputtering yield of this Si layer will be higher than in pure Si because of the higher mass of the underlying Ti atoms. To maintain the surface enrichment of Si during ion etching, the diffusivity of Si through the $TiSi_2$ layer must be high enough to replenish the Si atoms which are lost by sputtering. As discussed above, this replenishment is possible at temperatures of 500–700 °C, for which the dominant diffusion path is along grain boundaries in the $TiSi_2$ layer.[9] A schematic diagram of the sputtering process is shown in Fig. 6. For temperatures below 400 °C, the silicide layer is etched by normal sputtering. At high temperature (500–700 °C), the thickness of the silicide layer remains almost unchanged during sputtering as it moves into the underlying silicon.

To conclude, we have shown that ion etching of a layer of $TiSi_2$ on Si at elevated temperature is characterized by highly selective sputtering of Si. The combination of high Si diffusivity and low ion energy allows almost 100% selective removal of Si from the surface. This is a general mechanism for highly selective sputtering in multicomponent materials.

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[1] J. Bohdansky, H. Lindner, E. Hechtl, A. P. Martinelli, and J. Roth, Nucl. Instrum. Methods B **18**, 509 (1987).
[2] J. Fine, T. S. Andreadis, and F. Davarya, Nucl. Instrum. Methods **209**, 521 (1983).
[3] M. Shikata and R. Shimizu, Surf. Sci. **97**, L 363 (1980).
[4] Th. Wirth, V. Atzrodt, and H. Lange, Phys. Status Solidi A **82**, 459 (1984).
[5] K. Morita, H. Ohno, M. Hayashibara, and N. Itoh, Nucl. Instrum. Methods B **2**, 596 (1984).
[6] S. Motakef, J. M. E. Harper, F. M. d'Heurle, T. A. Gallo, and N. Herbots, J. Appl. Phys. **70**, 2660 (1991).
[7] F. M. d'Heurle, P. Gas, I. Engström, S. Nygren, M. Östling, and C. S. Petersson, IBM Res. Rep. RC 11151 (No. 50067) (1985).
[8] R. Beyers and R. Sinclair, J. Appl. Phys. **57**, 5240 (1985).
[9] I. J. M. M. Raaijmakers, Ph.D. thesis, University of Technology Eindhoven, The Netherlands, 1988.
[10] N. Matsunami, Y. Yamamura, Y. Itikawa, N. Itoh, Y. Kazumata, S. Miyagawa, K. Morita, and R. Shimizu, IPPJ-AM-14, Institute of Plasma Physics, Nagoya University, Japan (1980).
[11] V. Hinkel, L. Sorba, H. Haak, K. Horn, and W. Braun, Appl. Phys. Lett. **50**, 1257 (1987); F. M. d'Heurle and O. Thomas, Appl. Phys. Lett. **52**, 2269 (1988).
[12] R. Kelly and A. Oliva, Nucl. Instrum. Methods B **13**, 283 (1986).

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