# Point defects in Si after formation of a TiSi$_2$ film: Evidence for vacancy supersaturation and interstitial depletion

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The influence of TiSi$_2$ formation on native Si point defects has been studied at temperatures between 800 and 890 °C. Sb and B in doping superlattices were employed to trace point defect behavior. Formation of TiSi$_2$ at 890 °C gives rise to an interface root-mean-square (rms) roughness of 22 nm. Ambiguities in the interpretation of the data arising from possible secondary ion mass spectroscopy artifacts due to sputtering through such a rough interface were avoided by etching the TiSi$_2$ film and replanarizing the Si surface. A rms roughness of 0.05 nm was obtained, as checked by atomic force microscopy and cross-sectional transmission electron microscopy. We observed an enhancement in Sb diffusion and retardation of B diffusion over control samples without TiSi$_2$. This indicates a vacancy supersaturation and an interstitial depletion in the Si due to the presence of the silicide. Possible mechanisms of vacancy creation and interstitial depletion are discussed. © *1996 American Institute of Physics*. [S0003-6951(96)04212-6]

Titanium silicide (TiSi$_2$) has become a preferred material for ohmic contacts in integrated circuits (ICs) because of its low resistivity, resistance to electromigration, and its ability to self-align.[1] However, the effect of the growth of the silicide and subsequent post silicidation anneals on the population of intrinsic point defects has not been accurately characterized. This is an important issue because point defects play a dominant role in the diffusion of the common substitutional dopants in silicon.[2] As device dimensions shrink, prediction and control of dopant diffusion becomes crucial.

Direct measurement of the relative amounts of intrinsic point defects present in Si during and after processing is impossible. Therefore, indirect means of determining the relative size of the point defect population have been developed. Antimony has been shown to diffuse by a vacancy assisted mechanism and boron by an interstitialcy mechanism.[3,4] Hence, observation of changes in the diffusivities of these dopants in Si doping superlattices (DSLs) yield depth profiles of Si vacancies and interstitials.[5] This is the method utilized in the work reported in this letter. Previous reports of the impact of silicidation on Si point defects have suffered from silicide-induced roughening of the interface, resulting in secondary ion mass spectroscopy (SIMS) artifacts.[6–8] We have avoided this problem by replanarization of Si by chemo-mechanical polishing (CMP) after etching off the silicide. Our results indicate that growth and annealing of a ~70 nm film of TiSi$_2$ leads to a vacancy supersaturation and an interstitial depletion in the underlying Si.

Doping superlattices were grown by low-temperature molecular beam epitaxy (LT MBE).[9] They consisted of six Sb or B doping spikes with 10 nm widths and peak centers spaced 100 nm apart. Each B spike had a concentration of 1.3×10$^{19}$/cm$^3$ while each Sb spike had a concentration of 1.0×10$^{20}$/cm$^3$. The shallowest spike was capped with 50 nm of Si. Transmission electron microscopy (TEM) and atomic force microscopy (AFM) samples were made from Czochralski grown *p*-type Si(100). The TEM and AFM samples were used to study interface roughening and polishing.

Prior to Ti deposition, all samples were cleaned in TCA, acetone, methanol, de-ionized (DI) water, 10:1 buffered oxide etch (BOE), and DI water. The samples were loaded into a sputtering chamber which was pumped down to a base pressure of 2×10$^{-9}$ Torr. The chamber was backfilled with argon to a pressure of 2×10$^{-3}$ Torr and 30 nm of 99.995% purity Ti was sputtered onto the surface. Three sets of samples were annealed in forming gas (97% N$_2$+3% H$_2$) for 1 h at either 800, 840, or 890 °C. The furnace anneals were selected to insure a reasonably large diffusion length for Sb, the only dopant that is known to diffuse by a vacancy-dominated mechanism.[3] While interface roughness prevents an exact measure of the film thickness, we estimate the thickness to be 70 nm from cross-section TEM (XTEM). Titanium disilicide C54 phase was confirmed by electron diffraction. Doping superlattice samples without a film were annealed concurrent with each temperature to provide a comparison. The silicide was removed by etching in dilute HF (25%) for 6 min. The samples were chemo-mechanically polished to replanarize the surface while removing minimal amounts of the underlying Si, as shown by SIMS. The XTEM measurements were performed at 200 keV with the incident beam parallel to the [110] zone axis using bright field images. Tapping mode was used in AFM measurements, with a resolution of 0.01 nm. Dopant concentration profiles were obtained by SIMS with 2 keV Cs$^+$ ions for Sb profiling, and O$_2^+$ ions for B profiling. Dopant diffusivities were extracted by analyzing each dopant spike separately as described in Refs. 10 and 11. The diffusion equation was

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solved with the process simulator PROPHET[11] accounting for concentration and electric field effects, which results in $D_B^{int}$ and $D_{Sb}^{int}$, the intrinsic diffusivities of B and Sb, respectively. Diffusion coefficients are of the form $D = D_x h[1 + \beta(m/n_i)]$, where $m$ is the hole (in the case of B doping) or electron (Sb doping) concentration, respectively, $h$ is a Fermi level-dependent factor, and $\beta = 3$ and $\beta = 70 \exp(-0.43 \text{ eV}/kT)$ for B and Sb, respectively. The fitting algorithm returns $D_x$ from which we calculate $D^{int} = D_x(1 + \beta)$. Errors in the diffusivities have been estimated using a Monte Carlo approach as described in Ref. 10.

The TiSi$_2$ films on the samples annealed at 840 and 890 °C islanded and all samples, including those annealed at 800 °C, had significant interface roughening.[12,13] This interface roughness must be removed before accurate SIMS measurements can be made. About 110 nm of Si were removed by the silicide growth and subsequent polishing, which was confirmed by SIMS measurements. To better quantify roughness, tapping mode AFM was performed on the wafer before any processing, a 890 °C annealed sample after the silicide had been etched but not polished, and the same sample after polishing. The samples had root-mean-square roughnesses of 0.12, 22, and 0.05 nm, respectively, showing that the polishing actually improves the surface quality of the as-received wafers. The DSL samples annealed without a film were polished to the same degree to insure that any point defects introduced from polishing would be present in both sets of samples, and therefore, any enhancement or retardation of diffusion in the silicided samples over the samples without a film is due only to the presence of the silicide.

Figure 1 shows representative SIMS depth profiles on the samples annealed at 840 °C. The diffusion of antimony is enhanced while that of boron is retarded. Note that the first spikes were lost due to etching and polishing. The samples annealed at 800 and 890 °C showed similar behavior. The diffusivity of B and Sb in silicided samples, normalized to the values in unsilicided samples, is shown in Fig. 2. The enhancement in $D_{Sb}$ and retardation of $D_B$ occurs through the deepest spike at 550 nm in both sets of samples. The relatively greater variation in Sb diffusivity and larger error bars arise from the fact that Sb diffuses over an order of magnitude more slowly than B. Since $D_{Sb}$ ($D_B$) is proportional to the time averaged vacancy (interstitial) concentration, the results of Fig. 2 show that Ti silicidation and annealing lead to a vacancy supersaturation and interstitial depletion.

Our data demonstrate unambiguously that the presence of TiSi$_2$ perturbs the point defect population in Si. Previous experiments have given rise to considerable controversy. Several authors have proposed that Ti silicidation causes a vacancy supersaturation, which our results support.[14,15] However, we did not observe any asymmetric broadening of dopant profiles seen by other authors after silicidation.[6-8] Also, the amount of enhancement in Sb diffusion in our work is much less than in a previous report.[6] In those works, the interface may have roughened, leading to artifacts in SIMS. In fact, our AFM measurements indicate roughness of the interface on the scale of ten's on nms, comparable to the actual diffusion distances for Sb. In contrast, we have avoided these ambiguities by etching the TiSi$_2$ film and
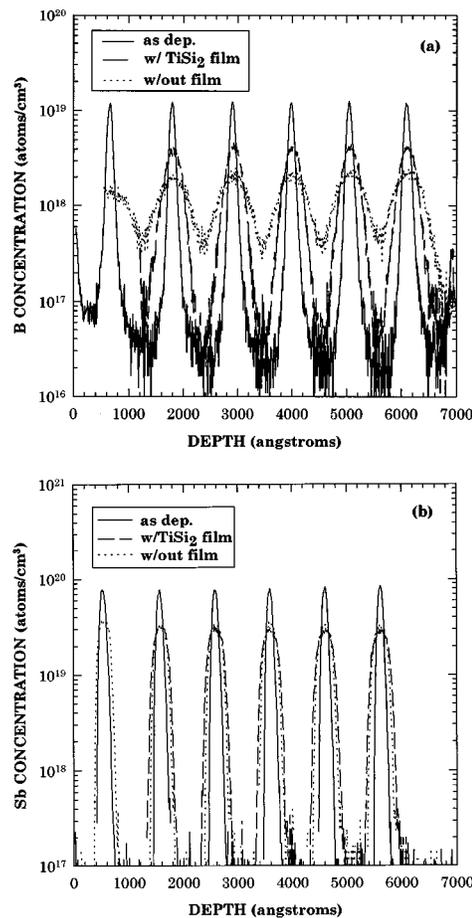


FIG. 1. Depth profiles of (a) B- and (b) Sb-doping superlattices before (solid line) and after anneals on samples with and without Ti. The samples were annealed at 840 °C for 1 h in forming gas.

chemo-mechanically polishing the Si surface.

A typical rapid thermal anneal (RTA) used to form the C54 phase of TiSi$_2$ involves a low-temperature anneal (e.g., 700 °C/10 s) to react the Ti with Si to form the C49 phase, followed by a selective etch to remove the unreacted Ti, with a higher temperature anneal (e.g., 735 °C/20 min) to convert
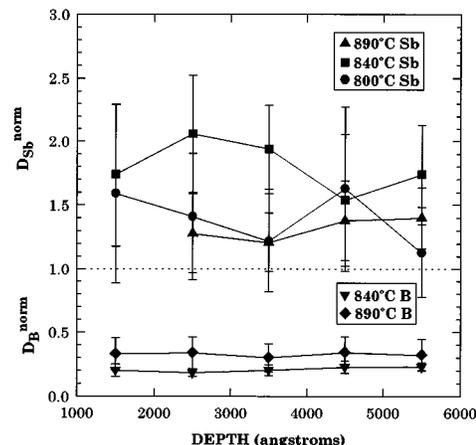


FIG. 2. Normalized B and Sb diffusivities in the TiSi$_2$ samples, where $D_B^{norm} = D_B^{int}$ (w/TiSi$_2$ film)/ $D_B^{int}$ (w/out TiSi$_2$ film) and $D_{Sb}^{norm} = D_{Sb}^{int}$ (w/ TiSi$_2$ film)/ $D_{Sb}^{int}$ (w/out TiSi$_2$ film).

the C49 phase to the low resistivity C54 phase.[16] However, this annealing sequence would result in equilibrium diffusion lengths too small to be detectable, making it impossible to measure the Sb diffusion coefficient in the control samples. Since little difference is seen in the diffusion behavior in our samples with a 90 °C temperature difference, we believe these results can be extrapolated to lower temperatures. However, we cannot rule out the possibility that the different morphology of TiSi$_2$ films produced by RTA-type processing may change the point defect behavior.

*A priori*, we cannot discriminate between vacancy injection and vacancy supersaturation due to interstitial depletion via $C_V C_I = C_V^* C_I^*$, where $C_V$ and $C_I$ are the concentrations of vacancies and interstitials after processing, respectively, and $C_V^*$ and $C_I^*$ are the equilibrium concentration of vacancies and interstitials. However, vacuum annealing experiments have shown that at 800 °C, an interstitial undersaturation does not lead to a vacancy supersaturation even after 10 h annealing time.[17] This indicates that the vacancy supersaturation is directly due to the presence of the TiSi$_2$ film.

Our results agree with the theory put forth by Wen *et al.*[15] that since Si is the diffusing species in the formation of TiSi$_2$, a vacancy must be left behind in the Si bulk. However, we cannot rule out other possible causes of the observed point defect behavior, such as the following: the release of stress in the silicide film by generation of Frenkel defects at the interface, with excess Si interstitials absorbed at the interface, the vacancies diffusing into the bulk and the resulting vacancy supersaturation depleting interstitials through Frenkel pair recombination; or the transformation of the silicide from a smooth film to islands causing a significant increase in the Si/TiSi$_2$ interface area; this increased surface area may act as a more efficient sink for interstitials and simultaneously enhance vacancy production. Determination of the exact mechanism by which Ti silicidation influences native point defects in Si requires further work.

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