

The influence of TiSi_2 and CoSi_2 growth on Si native point defects: The role of the diffusing species

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(Received 26 January 1996; accepted for publication 11 March 1996)

Boron- and Sb-doped superlattice samples have been used to investigate intrinsic point defects in Si after formation of TiSi_2 and CoSi_2 films from codeposited metal and Si. The as-deposited films had the compositions Ti, $\text{TiSi}_{0.8}$, $\text{TiSi}_{2.2}$, and $\text{CoSi}_{0.8}$. After annealing in argon for 1 h at 850 °C, the films formed TiSi_2 and CoSi_2 , respectively. All samples showed the same slight interstitial undersaturation and vacancy supersaturation. Since TiSi_2 and all its precursor phases form completely by Si diffusion and the $\text{CoSi} + \text{Si} \rightarrow \text{CoSi}_2$ transformation occurs by Co diffusion, this indicates that the diffusing species during film growth is not the determining factor in the point defect perturbation in the Si substrate. © 1996 American Institute of Physics. [S0003-6951(96)03820-X]

The diffusion of common dopants in Si is mediated by Si self-interstitials and vacancies.¹ Many processing steps during the manufacture of Si integrated circuits modify the native point defect population. Thus crucial device parameters are set by the interaction between Si native point defects and dopant atoms. Quantitative knowledge of these modifications is essential for predicting device performance during the device and process design phase.

Titanium and cobalt disilicides (TiSi_2 and CoSi_2) exhibit low resistivity, resistance to electromigration, and the ability to self-align,² they are commonly used to form ohmic contacts. We have recently established that the presence of a TiSi_2 film on Si during annealing results in a vacancy supersaturation and an interstitial undersaturation.³ Nevertheless, the mechanism by which silicide films effect a perturbation in the point defect population in Si has remained elusive. All the precursor phases of TiSi_2 , as well as TiSi_2 form by Si diffusing into Ti.⁴ Wen *et al.*⁵ have suggested that these Si atoms leave behind vacancies in the substrate, causing a vacancy supersaturation. The formation of CoSi_2 from CoSi proceeds via diffusion of metal into the Si substrate.⁶ This process should therefore inject interstitials. We have explored this theory by annealing TiSi_x and CoSi films with Si contents ranging from Si deficient ($x=0$) to Si rich ($x > 2.0$). In each case we measured the change in the native point defect population after film formation and annealing. All cases resulted in a slight vacancy supersaturation and interstitial undersaturation, indicating that the observed point defect perturbation is not linked to the diffusing species.

We used the diffusion of dopant atoms to track changes in the point defect population. Antimony has been shown to diffuse by a vacancy assisted mechanism and boron by an interstitialcy assisted mechanism.^{7,8} By observing changes in the diffusivities of these dopants in doping superlattices

(DSLs) we obtain depth profiles of Si vacancies (Sb) and interstitials (B).⁹ Growth and anneal of these silicide films at these times and temperatures result in a rough interface between the silicide and Si. We have eliminated the possibility of SIMS artifacts arising from sputtering through such a rough interface by chemically etching off the silicide and chemo-mechanically polishing the underlying Si.³ Doping superlattices were grown by low-temperature molecular beam epitaxy (LT-MBE) on float zone Si(100) wafers.¹⁰ They consisted of six Sb or B doping spikes with 100 Å widths, and peak centers spaced 1000 Å apart. Each Sb spike had a concentration of $1 \times 10^{20}/\text{cm}^3$ while each B spike had a concentration of $2 \times 10^{18}/\text{cm}^3$. The shallowest spike was capped with 500 Å of Si.

Prior to metal deposition, all samples were cleaned by a dilute HF (1:20) dip. The samples were loaded into an ultra-high vacuum (UHV) MBE chamber that was pumped down to a base pressure of 1×10^{-10} Torr. Titanium or Co of 99.995% purity and Si were coevaporated in separate depositions. Rutherford backscattering spectrometry gave compositions of Ti, $\text{TiSi}_{0.8}$, $\text{TiSi}_{2.2}$, and $\text{CoSi}_{0.8}$, respectively, and densities of 1.1×10^{17} Ti atoms/cm² (Ti only sample), 1.2×10^{17} Ti atoms/cm², and 9.8×10^{16} Si atoms/cm² ($\text{TiSi}_{0.8}$), 1.3×10^{17} Ti atoms/cm² and 2.8×10^{17} Si atoms/cm² ($\text{TiSi}_{2.2}$), and 2.4×10^{17} Co atoms/cm² and 1.9×10^{17} Si atoms/cm² ($\text{CoSi}_{0.8}$). Anneals were performed for 1 h at 850 °C in 99.95% purity argon cooled by a mixture of dry ice and acetone prior to furnace entry to prevent water intrusion. The annealed films were checked by cross-sectional transmission electron microscopy (XTEM), phases were confirmed by electron diffraction on plan view TEM samples (PTEM), and elemental analysis of the films was performed by Auger electron spectroscopy (AES). The resulting TiSi_2 films were all C54 phase while the CoSi_2 film was cubic. With the exception of the $\text{TiSi}_{2.2}$ film, a thin $\text{TiO}_x\text{N}_{1-x}$ film formed on top of the silicide [Fig. 1(a)]. The $\text{TiO}_x\text{N}_{1-x}$ film was ~200 Å thick while the TiSi_2 films were about 600 Å

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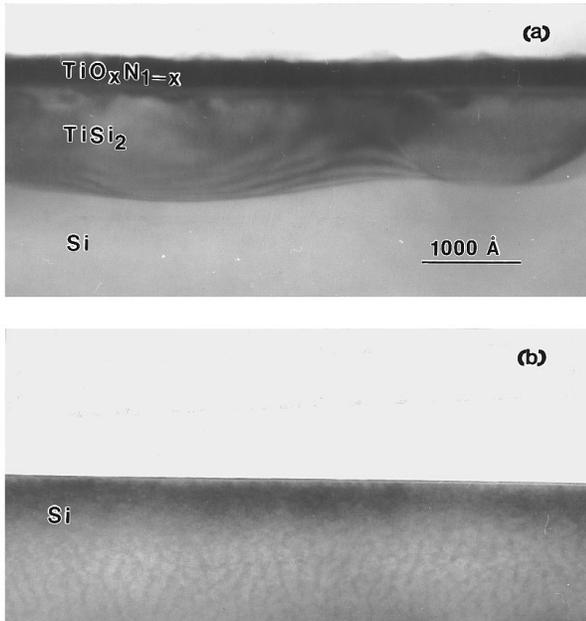


FIG. 1. (a) Cross sectional TEM micrograph after annealing; the sample had only Ti deposited (no Si); (b) the same sample after chemically etching off the film and chemo-mechanical polishing.

thick. The $\text{TiO}_x\text{N}_{1-x}$ formation is a result of impurities in the argon gas, and is typically seen when annealing in this ambient.^{11,12} The CoSi_2 film did not have any other phases. A subsequent paper will describe the composition, morphology, and interface roughness of the films in more detail [to be published in J. Appl. Phys.]. The silicides were removed by chemically etching in a dilute HF solution (25%), followed by chemo-mechanical replanarization of the underlying Si [Fig. 1(b)].³ Dopant concentration profiles were obtained by secondary ion mass spectrometry (SIMS). Dopant diffusivities were extracted by analyzing each dopant spike separately as described in Ref. 13. The diffusion equation was solved with the process simulator PROPHET accounting for concentration and electric field effects, which results in D_B^{int} and $D_{\text{Sb}}^{\text{int}}$, the intrinsic diffusivities of B and Sb, respectively.¹⁴ 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 $D^{\text{int}} = D_x(1 + \beta)$. Errors in the diffusivities have been estimated using a Monte Carlo approach.¹³

Figure 2 shows a representative SIMS depth profile. The diffusivity of Sb is enhanced in the sample with the TiSi_2 film compared to a sample annealed at the same time without Ti. Note the loss of the first doping spikes in the sample due to etching and polishing. Figure 3 shows the B and Sb intrinsic diffusivities in all the silicided samples, normalized to the diffusivities in the corresponding samples without a film. The larger error bars for the Sb DSL samples are a result of D_{Sb} being an order of magnitude smaller than D_B . Since $D_{\text{Sb}}(D_B)$ is proportional to the time averaged vacancy (interstitial) concentration, the presence of TiSi_2 and CoSi_2

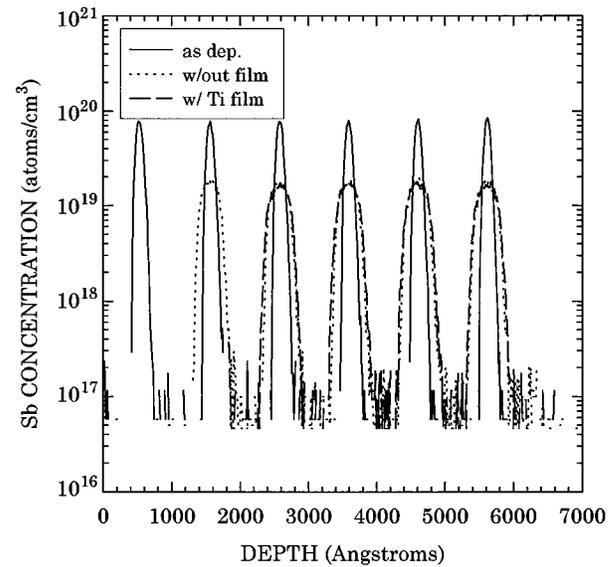


FIG. 2. Representative SIMS depth profile of the Sb DSLs, comparing the sample annealed with a film, no film, and the as-deposited samples. The sample with a film had Ti (only), as-deposited.

films from co-deposited metal and Si leads to a slight interstitial undersaturation and slight vacancy supersaturation in the Si substrate. This result is independent of the Si content of the as-deposited metal films.

The vacancy supersaturations and interstitial depletions are caused by the presence of the films, and are not due to generation or annihilation via $C_V C_I = C_V^* C_I^*$. Vacuum annealing experiments have shown that after 10 h at 800 °C, an interstitial undersaturation does not lead to a vacancy supersaturation.¹⁵ Gold and platinum diffusion experiments also indicate that recombination of vacancies and interstitials is inefficient at temperatures below 850 °C.^{8,16} These results agree with the conclusion of Honeycutt,¹⁷ who proposed that these silicides can act as efficient interstitial sinks as well as vacancy sources.

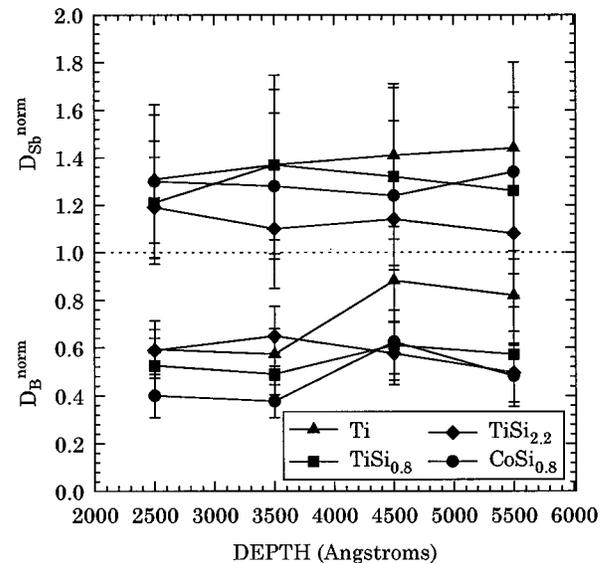


FIG. 3. Plot of the diffusivities of B and Sb, where $D_B^{\text{norm}} = D_B^{\text{int}}(\text{w/film})/D_B^{\text{int}}(\text{w/out film})$ and $D_{\text{Sb}}^{\text{norm}} = D_{\text{Sb}}^{\text{int}}(\text{w/film})/D_{\text{Sb}}^{\text{int}}(\text{w/out film})$.

Since the precursor phases of TiSi_2 as well as TiSi_2 itself form by Si diffusion, TiSi_2 formed from codeposited TiSi_x with $x=0$ and $x=0.8$ should form completely by Si diffusion, leaving vacancies in the Si substrate, as actually observed.⁵ However, for $x=2.2$, no Si from the substrate is consumed by the reaction, hence the point defect concentrations in the substrate should remain unchanged, contrary to the experimental observation. The two precursor phases of CoSi_2 , namely Co_2Si and CoSi , form by Co and Si diffusion, respectively, while CoSi_2 forms by Co diffusion.⁶ Thus, the formation of CoSi_2 starting from $\text{CoSi}_{0.8}$ should be dominated by Co diffusion with a smaller amount of Si diffusion. Given that recombination of interstitials and vacancies is slow at the annealing temperature, we would consequently expect both interstitial and vacancy excess. However, the experiment results in an interstitial deficit. The facts that (1) the magnitude of the point defect perturbation is approximately the same for all samples; (2) growth is complete in both films in less than 1 min at 850 °C while our measurements were taken after a 1 h anneal;^{18,19} and (3) TiSi_2 and CoSi_2 have different formation kinetics and yet have the same point defect results in our samples,^{5,6,11,19} argue strongly against the theory that the diffusing species and film growth itself are the primary mechanisms for the observed point defect perturbation. In our previous publication, we speculated on possible mechanisms for the point defect perturbation.³ This result leaves the possibilities that stress release of the film, morphological changes in the film, or other mechanisms effect the change in point defect population due to the presence of a TiSi_2 film.

The authors wish to thank C. S. Rafferty for many dis-

cussions and the provision of PROPHET, T. Boone for substrate preparation, and Eric Lambert for the Auger profiling. This work was partially supported by SEMATECH.

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