Manipulation of the Ti/Si reaction paths by introducing an amorphous Ge interlayer

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Evolution of the Ti/*a*-Ge/Si trilayer reactions has been investigated using transmission electron microscopy and Auger electron spectroscopy. Instead of amorphous phase formation, as usually observed in the Ti/Si bilayer reaction, the crystalline Ti_6Ge_5 is the first phase observed during the reaction. Preceding the equilibrium C54-Ti(Si,Ge)$_2$, a substitutional solid solution type C49-Ti(Si,Ge)$_2$ forms upon annealing at 550–600 °C, regardless of the replacement of amorphous phase by the crystalline phase. The C49-to-C54 polymorphic transformation occurs at ~650 °C. The reaction path is also correlated with the change in film resistance obtained from a four-point sheet resistance measurement.

Prediction and control of thin film reaction paths are fundamental subjects in thin film kinetics and materials physics. By properly changing chemistry at reacting interfaces, atomic mobilities and chemical reactivities of diffusing elements can be adjusted, and interfacial reaction paths and reaction products may be modified. The technologically useful, low resistivity $TiSi_2$ with a C54 structure (face-centered orthorhombic) is often produced by the reaction of Ti film with Si substrate. This reaction proceeds via a complicated path, i.e., Ti/Si→amorphous silicide→C49-$TiSi_2$ (base-centered orthorhombic, high resistivity)→C54-$TiSi_2$.[1,2] The appearance of the metastable C49 disilicide (typically at 500–600 °C) raises the processing temperature for obtaining the desirable equilibrium C54 polymorph (⩾650 °C).[3,4]

Much effort has been made to understand why and how this C49 phase forms in order to suppress its nucleation.[5,6] Previous studies[7] indicate that the C49 disilicide has a lower nucleation energy barrier as compared with the C54 phase and results from the interfacial reaction between the amorphous silicide and the Si. As the amorphous silicide is a major component for the C49 phase formation and is a thermodynamically metastable phase formed via solid-state amorphization,[8] it is suspected that its appearance may facilitate the nucleation of the C49-$TiSi_2$ by modifying interfacial energy and thus reducing energy barrier for nucleation. This conjecture seems further supported by a recent discovery of the existence of a C49 structure of $TiGe_2$ during the crystallization of a coevaporated amorphous $Ti_{0.33}Ge_{0.67}$ alloy.[9] On the other hand, neither an amorphous germanide nor the C49-$TiGe_2$ has been found in the Ti/Ge thin film couples.[10,11] These various results suggest that formation of the C49 phase depend upon the pre-existence of the amorphous phase. In other words, the C49 phase may be bypassed if the amorphous phase can be somehow eliminated, as in the case of Ti/Ge bilayer reactions where Ti/Ge→Ti_6Ge_5 →C54-$TiGe_2$.[10]

In this letter, we report on modification of the Ti/Si reactions paths leading to the formation of C54 phase by utilizing a thin sacrificial Ge interlayer. The Ge layer was chosen because of no equivalent to the amorphous silicide in the Ti/Ge bilayer reaction and similar properties of Si and Ge. In addition, the use of a Ge layer between Ti and Si also has potential applications in ultra-large-scale integration (ULSI) technology for ultrashallow junctions by minimizing the Si consumption during self-aligned silicidation (SALICIDE) process.[12] A good knowledge of the reaction sequences in this process is very useful in order to successfully carry out the process and controllably form desired junctions.

Single crystalline Si (100) wafers were used in the study. The Si substrates were cleaned chemically using a standard procedure followed by dipping in a dilute HF solution prior to loading into a molecular beam epitaxy system with a base pressure of 5×10^{-11} Torr. Following an *in situ* thermal desorption at >850 °C for 10 min, the substrate temperature was lowered to and held at 40 °C. About 200-Å-thick Ge and 500-Å-thick Ti films were sequentially grown onto the reconstructed (2×1) clean Si substrate as verified by reflected high-energy electron diffraction (RHEED). The pressure was maintained below 4×10^{-10} Torr during deposition. The thicknesses of these films were chosen in such a way that some of the Ti film would be left after the entire Ge layer was consumed. The samples were subsequently annealed in a high vacuum furnace (5×10^{-8} Torr) at temperatures over 400 to 750 °C for 30 min. The reaction paths and products were studied by cross-sectional transmission electron microscopy (XTEM) and x-ray diffraction (XRD). Chemical composition was analyzed using energy-dispersive x-ray microanalysis (EDX) as well as Auger electron spectroscopy. The sheet resistance of samples was measured *ex situ* using a standard four-point apparatus.

The as-deposited sample was first characterized using XRD and electron diffraction. The Ge film was found to be

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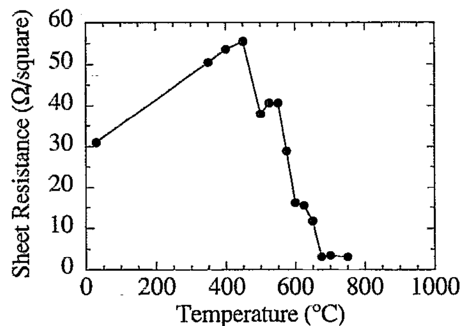

FIG. 1. The sheet resistance of the films measured after thermal annealing at different temperatures using a standard four-point apparatus.

amorphous, while the Ti film showed a polycrystalline structure. These results are consistent with the RHEED observations during deposition. Figure 1 shows a plot of sheet resistance of the samples measured after annealing treatment at different temperatures. As expected from the figure, no significant reactions occurred at the Ti/*a*-Ge interface after annealing at temperatures below 400 °C. This is confirmed by TEM and XRD analyses. After annealing at 400 °C for 30 min, the amorphous Ge layer was found to transform into an epitaxial film on the Si substrate via solid phase epitaxial growth [see Fig. 2(a)]. The resistance plot exhibits three distinctive drops at about 450, 550, and 650 °C, respectively. These abrupt decreases in film resistance signify major reactions beginning at these temperatures. To identify reaction paths and phases resulting from the reactions, samples annealed at different temperatures were examined using XTEM and XRD. Selected samples were also examined by plan-view TEM.

Shown in Fig. 2(a) is an XTEM micrograph of a sample after 400 °C, 30-min anneal. A continuous layer of crystalline phase of about 80 Å thick is seen at the Ti/epitaxial Ge (epi-Ge) interface, as revealed by the Moiré fringes and contrast in the layer. Electron diffraction and EDX analyses indicate that the crystalline phase is a Ti-rich Ti_6Ge_5. The formation of this compound was previously reported as the first crystalline phase in the Ti/*c*-Ge reactions from a Rutherford backscattering spectrometry (RBS) study.[10,11] Our results confirm this conclusion and indicate that nucleation of this

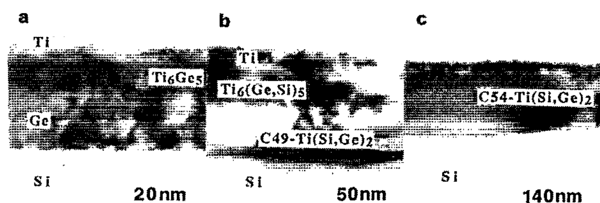

FIG. 2. Cross-sectional TEM images of the samples annealed at (a) 400 °C, 30 min. A thin layer of Ti_6Ge_5 is observed to form at the Ti/epi-Ge interface, (b) 575 °C, 30 min, showing the formation of C49-$Ti(Si,Ge)_2$ as a reaction product between $Ti_6(Ge,Si)_5$ and Si, and (c) 700 °C, 30 min. The high resistivity, metastable C49-$Ti(Si,Ge)_2$ has transformed to the low resistivity, equilibrium C54-$Ti(Si,Ge)_2$.

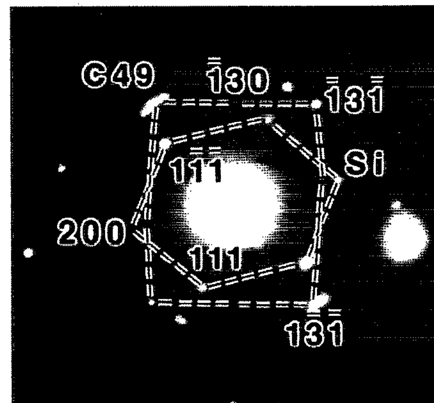

FIG. 3. A selected area electron diffraction pattern, showing the existence of the C49-$Ti(Si,Ge)_2$. In the figure, the [311] zone axis pattern of the C49 phase is superimposed on the Si[110] zone axis pattern. The extra spots are due to other nearby C49 grains.

phase occurs at temperatures lower than 450 °C due to higher resolution of TEM compared with RBS techniques. Both interfaces of the Ti_6Ge_6 layer are fairly abrupt, suggesting that the growth proceeds by a diffusion-controlled mechanism. Heat treatment at 475–550 °C for 30 min resulted in further growth of this phase at the expense of both Ti and Ge. It is found that the Ti_6Ge_5 grew until all the epi-Ge was consumed, but there were still some Ti left at this stage. In this temperature range, some Si atoms are expected to diffuse out and are incorporated into the growing germanide to form $Ti_6(Ge,Si)_5$, as revealed by EDX.

During annealing at 550–600 °C, the film resistance decreases rapidly, indicating the formation of a low resistivity phase. XRD measurements revealed a few new peaks which could not be unambiguously indexed because of the peak shifts resulting from the Ge substitution. Further phase identification was performed using TEM and Auger depth profiling. As shown in Fig. 2(b), this new phase is $Ti(Si,Ge)_2$ with a base-centered orthorhombic structure, being identical to C49-$TiSi_2$. The structure evidence for the formation of C49-$Ti(Si,Ge)_2$ was provided by electron diffraction analysis and is presented in Fig. 3. The diffraction patterns match well with the computer-simulated C49 [311] and Si [110] zone axis patterns. EDX analysis and Auger depth profiling confirm the stoichiometry of the C49 phase with some of the Si substituted by Ge. Such a substitutional solid solution type of C49-$Ti(Si,Ge)_2$ has previously been observed.[9] It is worth pointing out that similar to C49-$TiSi_2$ the Ge-containing C49 phase is also heavily faulted along the **b** direction of the unit cell.[13] The last resistance change in the Fig. 1 is straightforward and is due to the C49-$Ti(Si,Ge)_2$-to-C54-$Ti(Si,Ge)_2$ polymorphic transformation. Figure 2(c) shows the C54-$Ti(Si,Ge)_2$ film formed by annealing at 700 °C for 30 min. Except for a surface oxide layer, the C54 phase is quite uniform through the entire film. The electrical resistivity of the film was estimated to be ~30 $\mu\Omega$ cm.

The results obtained in this work reveal some interesting points. The use of a Ge interlayer avoids the formation of an amorphous phase, which always appears first in the Ti/Si

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bilayer reaction, and thereby alters the reaction path, leading to the first crystalline reaction product Ti_6Ge_5. Based upon the previous report by Hong *et al.*,[9] the amorphous phase seems a prerequisite precursor for the C49 phase formation, where local chemical short-range ordering may promote its nucleation. Due to the replacement of the amorphous phase by the crystalline phase, it is interesting to see which way further reactions would lead to; direction formation of the C54 phase without going through the C49 phase first or the same sequence as in the Ti/Si system. Thus the role of the amorphous phase in the C49 phase nucleation may be addressed. Our results have clarified this issue and have clearly shown that the C49-$Ti(Si,Ge)_2$ actually appears as a reaction product between $Ti_6(Ge,Si)_5$ and Si, and precedes the C54-$Ti(Si,Ge)_2$. The formation of the C49 phase is believed to be due to the same kinetic reason; a lower energy barrier for its nucleation as compared to the C54 polymorph.

In conclusion, studies of the Ti/*a*-Ge/Si trilayer reactions have been presented. Instead of amorphous phase formation, Ti_6Ge_5 is the first phase observed during reaction. The C49-$Ti(Si,Ge)_2$ phase is not bypassed and forms prior to its polymorphic counterpart C54-$Ti(Si,Ge)_2$. From a technological viewpoint, by using a sacrificial Ge layer of various thickness, the Si consumption can be minimized and the junction depth can be adjusted to meet the needs for ultra-large-scale integrated circuits. Furthermore, because of the high selectivity of Ge growth by chemical vapor deposition,[12] the standard two-step annealing process developed for the SALICIDE technology can be used in conjunction with this metallization scheme without modification.

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