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Citation: Applied Physics Letters **70**, 2386 (1997); doi: 10.1063/1.118880 View online: http://dx.doi.org/10.1063/1.118880 View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/70/18?ver=pdfcov Published by the AIP Publishing

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Growth of TiSi₂ from codeposited TiSi_x layers and interfacial layers

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(Received 11 December 1996; accepted for publication 10 March 1997)

The silicide formation characteristics from composition profiles created on Si by codepositions was investigated. It was shown that a thin interfacial amorphous TiSi_x layer, with $x \sim 0.5-1$, deposited between Si and the Ti film led to a significant reduction in the observed $C49 \rightarrow C54 \text{ TiSi}_2$ transformation temperature. The presence of the amorphous interfacial TiSi_x layer slowed down the initial silicidation rate, but promoted the nucleation of the final $C54 \text{ TiSi}_2$ phase. Predeposition and preannealing were also found to facilitate the growth of $C54 \text{ TiSi}_2$, as was growth from codeposited full TiSi_x layers with Ti-rich compositions. The efficacy of the (interfacial) TiSi_x layer was demonstrated for different temperature ramp rates and for a variety of substrates including undoped α -Si, preamorphized n^+ -Si, and preamorphized p^+ -Si. But this effect was found to be absent on single crystal Si. Possible mechanisms of the observed effects were discussed. © 1997 American Institute of Physics. [S0003-6951(97)04318-0]

Ti silicide is presently the most widely used self-aligned silicide (salicide) for high-performance ultralarge scale integration (ULSI) devices. However, it is difficult to process devices with a gate length shorter than 0.25 μ m using the Ti salicide technology, because of the well-known problem with the polymorphic transformation, C49-TiSi₂ \rightarrow C54-TiSi₂, in narrow silicide lines.¹ The reaction between a Ti thin film and a Si substrate starts with the formation of a precursor interfacial amorphous silicide layer with a graded composition.^{2,3} The C49-TiSi₂ phase is then nucleated at the interface between the precursor amorphous silicide layer and Si.3,4 Subsequently, the nucleation of the desired, lowresistivity, C54-TiSi₂ phase is believed to take place at multiple grain boundaries of the C49 TiSi₂ film.^{3,5} It is the low density of these favorable sites in narrow C49-TiSi2 lines which leads to the observed linewidth dependence. By adding impurities, it has been shown that the C49-C54 transformation temperature can be lowered.^{6–8}

Recently, the combination of high temperature sputtering (HTS) of Ti (~450 °C) and the use of preamorphized (PAM) Si was shown to significantly reduce the C54-TiSi₂ transformation temperature on narrow lines.^{9,10} The easier nucleation of the C54-TiSi2 phase was speculated to arise from the formation of a thick (~6 nm) α -TiSi_x layer, during the HTS process, at the interface between PAM Si and the sputtered Ti. In separate experiments,¹¹ it was shown that deposition of Ti at temperatures (\geq 500 °C) above the amorphous-to-crystalline transition temperature¹² for Si-rich $TiSi_{r}$ led to the direct nucleation of the C54-TiSi₂ phase on α -Si. The easy nucleation of the C54 phase, in the latter case, was attributed to an avoidance of the amorphous TiSi_x phase. These apparently different effects of the amorphous TiSi, interfacial layer, though not necessarily mutually conflicting, pointed to the complexity of the Ti silicide problem and the importance of understanding the roles played by the amorphous $TiSi_x$ interfacial layer. In this work, the silicide reaction of amorphous TiSi_x layers and interfacial layers on amorphous and crystalline Si was studied. A novel dependence of the formation of the C54-TiSi₂ phase on the composition of the TiSi_x layer was discovered.

Si(100) wafers, implanted with either 70 keV $3E15/\text{cm}^2$ As or 30 keV $3E15/\text{cm}^2$ BF₂, annealed at 900 °C for 10 min, preamorphized (PAM) with a 70 keV $3E14/\text{cm}^2$ As implantation were used in the majority of these experiments. Oxidized Si wafers with a 200-nm-thick plasma-enhanced chemical vapor deposition (PECVD)grown amorphous-Si layer and other types of wafers were also used. Substrates were cleaned chemically and given a dilute HF etch before loading in an ultrahigh vacuum (UHV) system. Ti and Si were deposited using individually controlled e-beam sources. Throughout this article, a "1 nm* TiSi_r" is defined as a codeposited TiSi_r layer which contains the equivalent of 1 nm Ti. Anneals were done in the UHV chamber, without a break of vacuum, by resistively heating. Unless otherwise specified, a temperature ramp rate of $\sim 10^{\circ}$ C/s was used for these anneals.

A dependence of the the sheet resistance on the deposition temperature was found for silicide layers grown from the deposition of 15 nm Ti. After a 680 °C 10 s anneal, sheet resistances of 17 and 7.8 Ω/\Box were measured for Ti layers originally deposited on As-doped PAM Si at room temperature and at 460 °C, respectively. These results were in good agreement with the dependence on the deposition temperature observed previously, using inert gas sputtering, thicker Ti layers, and a nitrogen annealing ambient.¹⁰ Amorphous TiSi, interfacial layers were artificially recreated on PAM Si by codeposition at room temperature. Sheet resistances of TiSi₂ films grown with a 4 nm^{*} interfacial layer displayed a dependence on the composition of the interfacial layer, as shown in Fig. 1. With a Ti-rich TiSi_x , x = 0.5-1, a significant fraction of the silicide film was converted to the C54-TiSi₂ phase after a 30 s (RTA) at \sim 650 °C. Layers with no interfacial layer (x=0) or with a Si-rich TiSi_x interfacial layer remained largely in the C49-TiSi₂ phase, after the same anneal. Codeposited amorphous TiSi_x layers were found not to have a significant effect on the sheet resistance

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FIG. 1. Sheet resistances of Ti silicide layers grown from the depositions of $4 \text{ nm}^* \text{TiSi}_x$ and 11 nm Ti at room temperature and a 30 s RTA.

of TiSi₂ layers grown on single crystal Si substrate, under similar annealing conditions.

To determine the dependence of the silicide reaction on the thickness of the amorphous interfacial layer, codeposited $TiSi_x$ with x = 1.0 were used. Figure 2 shows planview transmission electron microscopy (TEM) images of TiSi₂ layers grown from interfacial layers with thicknesses of 0, 2, 4, and 6 nm^{*}. In these micrographs, the majority of grains with small sizes (≤ 50 nm) were C49-TiSi₂ and those with large grain sizes (≥ 200 nm) were mostly C54-TiSi₂ in nature. A clear increase in the C54-TiSi2 volume fraction was observed in these 650 °C-annealed films, when thin interfacial $TiSi_{1,0}$ layers were used. However, the dependence of the film microstructure on the thickness of the interfacial layer was not strong for TiSi_{1.0} interfacial layers over 2 nm* thick. TEM-observed formation characteristics of the C54-TiSi₂ phase were in good qualitative agreement with the sheet resistances measured in these films (see Fig. 2 caption).

Interfacial amorphous TiSi_x layers with different thicknesses and/or compositions were also generated by predeposition and preannealing. A small amount, t_A , of Ti was predeposited at room temperature on PAM Si and was preannealed at 460 °C for 5 min. This annealing condition



FIG. 2. Planview TEM images of TiSi_2 layers grown on As-doped PAM Si with $\text{TiSi}_{1,0}$ interfacial layer thicknesses of (a) 0, (b) 2, (c) 4, and (d) 6 nm^{*}, respectively. The measured sheet resistances were (a) 12.2, (b) 7.5, (c) 6.2, and (d) $6.7\Omega/\Box$, respectively.



FIG. 3. Sheet resistance of Ti silicide layers grown from preannealing of predeposited Ti films.

was known to lead to the growth of amorphous silicide at a Ti/Si interface without the nucleation of crystalline silicide phases. Epitaxial regrowth of the PAM layer was also known to be insignificant at this temperature. A Ti layer with a thickness of t_B (=15 nm- t_A) was then deposited at room temperature, and a final *in situ* RTA at 685 °C then completed the growth of the Ti silicide. As shown in Fig. 3, TiSi_x layers formed by preannealing were also effective in lowering the sheet resistance of the TiSi₂ layer. Preannealing the entire 15-nm-thick Ti layer, however, led to a sheet resistance which was higher than that from a layer grown without preannealing ($t_A=0$). When the predeposition and preannealing procedures were applied to silicide films grown on single-crystalline Si substrates, no reduction in the silicide sheet resistance was observed.

The formation of silicide layers from TiSi_x thin films, 15 nm* in thickness, codeposited at room temperature was studied. Results on PAM and singel crystal As-implanted Si, obtained after a 650 °C 30 s anneal were shown in Fig. 4. On PAM Si, the sheet resistance of a TiSi₂ film showed a strong dependence on the composition of the starting $TiSi_x$ layer. There was a rapid drop in the sheet resistance when a small fraction of Si was added to the Ti deposition. Ti-rich codepositions led to a nearly complete transformation to the C54-TiSi₂ phase, as evidenced by the low sheet resistance observed for TiSi_{0.25}. The higher sheet resistances for pure Ti (x=0) and Si-rich codeposited layer (x=2) was due to an incomplete transformation to the low-resistivity C54-TiSi₂ phase. On single crystal Si, the measured sheet resistances suggested that little C54-TiSi2 reaction had taken place for all the layers. The decrease of sheet resistance with x, observed on single crystal Si, was likely influenced by a decrease in dopant incorporation in the (majority C49-TiSi₂) silicide film.

Ti silicide layers grown on BF₂-implanted PAM Si by codeposition also displayed a dependence of their sheet resistances on the codeposition composition, as shown in Figs. 5 and 6. The formation of the C54-TiSi₂ phase was found to be easier with a starting composition of $x \sim 0.5-1$ than with pure Ti layers. When the temperature ramp rate was changed from 10 (RTA in Fig. 5) to 0.2 °C/s (slow ramp in Fig. 5), there was an increase in the sheet resistance. But a clear



FIG. 4. Sheet resistance of Ti silicide layers grown from the codeposition of 15 nm* TiSi_x at room temperature and annealing at 650 °C for 30 s. Results are plotted for layers grown on heavily As-doped single crystal Si and PAM Si.

dependence of the sheet resistance on the codeposition composition was still present using the very slow ramp rate. The microstructures of silicide layers grown on PAM Si, from codeposited TiSi_x were revealed by planview TEM in Fig. 6. Silicide films consisting of predominantly small C49-TiSi₂ grains were found from the annealing of a pure Ti layer, as shown in Fig. 6(a). The annealing of a nearly stoichiometric TiSi_x layer (x=2) led to predominantly C49-TiSi₂ grains, but with a larger average grain size, Fig. 6(c). C54-TiSi₂ grains were observed to occupy a high areal fraction only in the film grown from a codeposited TiSi_{1.0} layer, Fig. 6(b).

A thick (>3 nm^{*}) TiSi_x layer or interfacial layer was presently shown to lead to an easier $C49 \rightarrow C54$ -TiSi₂ phase transformation on amorphous Si. This observation strongly supported the attribution of the observed reduction in the C54-TiSi₂ nucleation temperature in the HTS process to the formation of a thick interfacial TiSi_x layer.¹⁰ It was also known that the initial silicidation rate was slowed down



FIG. 6. Planview TEM micrographs of TiSi₂ layers grown from 15-nm*-thick TiSi_x layers codeposited on BF₂-implanted PAM Si. Codeposition compositions were (a) x=0, (b) x=1.0, and (c) x=2.0

when an interfacial TiSi, layer was present.¹⁰ Even though the present results showed a dependence on the doping and annealing conditions, TiSi, layers with slightly metal-rich compositions, $x \sim .2 - 1$, generally led to the easiest formation of the C54-TiSi₂ phase. The absence of an effect on crystalline Si was suggestive that the amorphous Si-TiSi, interface was important for the enhanced nucleation of C54-TiSi₂. The precise role played by the TiSi_x layer is not clear at the present. The nucleation of C54-TiSi2 is expected to be enhanced from C49-TiSi2 films with a smaller average grain size, but direct evidence for a dependence of the grain size on the presence of (interfacial) TiSi, layer is presently lacking. It was suggested that the C49-TiSi₂ crystals grown from such an interfacial layer were more defective, making the ensuing transformation into the C54-TiSi₂ phase easier.¹⁰ Silicide thin films grown from α -TiSi_x could possibly have a higher compressive stress, thus favoring the nucleation of C54-TiSi₂. The transient formation of TiSi or metal-rich silicide phases could also have an effect on the disilicide reaction. In any event, the present results suggest the addition of a small amount of Si in the deposited Ti for easier salicide or polycide applications.

The authors thank F. Schrey for his assistance with the experiments.



FIG. 5. Sheet resistance of Ti silicide layers grown from 15 nm* TiSi_x codeposited at room temperature and annealed *in situ* for 30 s. Temperature was ramped to 650 °C using ramp rates of 0.2 and 10 °C/s.

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