

Effects of Mo-free $C_{40}Ti(Si_{1-x}Ge_x)_2$ precursors and the thickness of an interposed Mo layer on the enhanced formation of $C_{54}Ti(Si_{1-x}Ge_x)_2$

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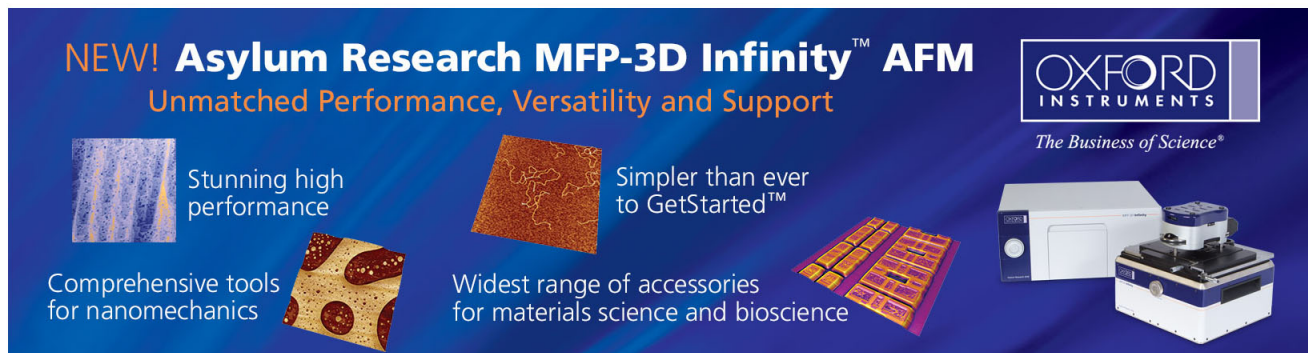
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Effects of Mo-free C40 $\text{Ti}(\text{Si}_{1-x}\text{Ge}_x)_2$ precursors and the thickness of an interposed Mo layer on the enhanced formation of C54 $\text{Ti}(\text{Si}_{1-x}\text{Ge}_x)_2$

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The effects of Mo-free C40 $\text{Ti}(\text{Si}_{1-x}\text{Ge}_x)_2$ precursors and the thickness of an interposed Mo layer between Ti films and $\text{Si}_{0.76}\text{Ge}_{0.24}$ substrates on the lowering of formation temperature of C54 $\text{Ti}(\text{Si}_{1-x}\text{Ge}_x)_2$ were studied. Metastable C40 $\text{Ti}(\text{Si}_{1-x}\text{Ge}_x)_2$ precursors were grown by pulsed KrF laser annealing. Upon rapid thermal annealing, the Mo-free C40 phase could not be directly transformed to the C54 phase without going through the C49 phase. When the thickness of the interposed Mo layer increased, up to 2.5 nm, the temperature at which the C54 phase was initially formed changed from 750 to 600 and then to 650 °C. The present result showed that with increasing Mo concentration in the reacted layer, the phase stability shifted from C54 to C40 and no C49 was observed. It seems that apart from the C40 template mechanism, the electron/atom ratio also plays an important role in the enhanced formation of the C54 phase. © 1999 American Institute of Physics. [S0003-6951(99)02048-3]

TiSi_2 has been widely used for Ohmic contacts and gate electrodes in ultra-large-scale integration (ULSI) devices because of its low resistivity, good thermal properties, and compatibility with the self-aligned silicidation process. TiSi_2 may exist either as the high-resistivity C49 phase or as the low-resistivity C54 phase.¹ For device applications, C54 TiSi_2 is preferred because of its low resistivity. The C49 phase generally forms first at temperatures ranging from 550 to 700 °C and then transforms to the C54 phase at temperatures above 750 °C. Fine line effects further raised the C49–C54 transformation temperature.² The morphological stability of the C54 phase during high-temperature annealing is crucial to the development of ULSI technology.²

Recently, it has been shown that the C49–C54 transformation temperature can be lowered by preamorphization of Si substrates before Ti deposition,^{3–5} ion implantation of Mo or W into Si substrates before Ti deposition,^{6,7} and deposition of an interposed layer of refractory metals or alloys between the Ti film and Si substrate, respectively.^{8–12} The enhanced formation of the C54 phase by preamorphization of Si substrates or Mo or W ion implantation is attributed to the increased nucleation sites of the triple junctions in the C49 phase.^{10,13,14} The enhanced growth of the C54 phase by the interposition of a refractory metal layer may be explained as due to the formation of the C40 phase which acts as a template for the growth of the C54 phase.^{7–9,12} Recently, it has also been reported that the phase stability of TiSi_2 changes from C49 to C54 and then to C40, being facilitated by increasing the electron/atom ratio.^{15,16} Therefore, the mechanism responsible for the enhanced formation of the C54

phase by interposing the refractory metal to Ti films still remains to be clarified.

$\text{Si}_{1-x}\text{Ge}_x$ material offers the promise of greater carrier mobility and band-gap engineering, and hence, has potential applications in high-speed electronic and optoelectronic devices.¹⁷ The formation of metal– $\text{Si}_{1-x}\text{Ge}_x$ Ohmic or rectifying contacts is required for device applications. Therefore, the motivation for studying the Ti/Si system is favorably transferred to the Ti/ $\text{Si}_{1-x}\text{Ge}_x$ system.^{18–23} In the interfacial reactions of Ti/ $\text{Si}_{1-x}\text{Ge}_x$, the modes of agglomeration and Ge segregation of the germanosilicide could be generally regarded to occur after higher-temperature annealing. It is desired that reducing the C54 transformation temperature would improve the aforementioned phenomena. In the present study, therefore, we interposed a Mo layer to the Ti/ $\text{Si}_{0.76}\text{Ge}_{0.24}$ system to study its thickness effect on lowering the C54 transformation temperature. In addition, Mo-free C40 $\text{Ti}(\text{Si}_{1-x}\text{Ge}_x)_2$ films prepared by pulsed KrF laser annealing were also provided to examine whether they could enhance the growth of the C54 phase or not on subsequent rapid thermal annealing. From these results the viable mechanisms responsible for the enhanced formation of the C54 phase could be elucidated.

Strained and partially relaxed $\text{Si}_{0.76}\text{Ge}_{0.24}$ films with thicknesses of 100 and 150 nm, respectively, were grown at 550 °C in an ultra-high-vacuum chemical-vapor deposition system. Ti films about 25 nm thick were deposited onto the $\text{Si}_{0.76}\text{Ge}_{0.24}$ films at a rate of 0.1 nm/s in an electron-gun deposition system. The base pressure was about 1.0×10^{-6} or 1.0×10^{-10} Torr. Rapid thermal annealing was conducted at a temperature of 500–800 °C for 30 s in N_2 . Pulsed KrF laser annealing was performed in a vacuum around 2.0×10^{-2} Torr. The pulse length was 14 ns. The laser beam was focused onto an area of $4 \times 4 \text{ mm}^2$. Phase formation and

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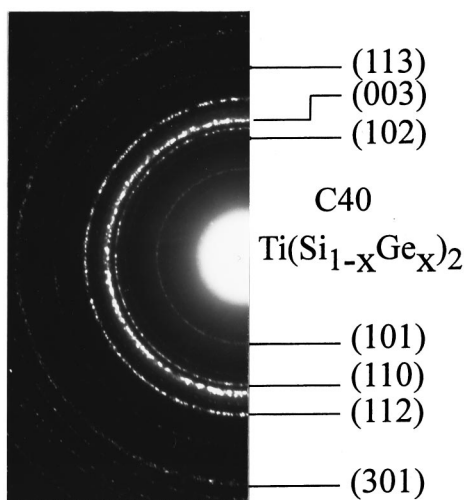


FIG. 1. DP of the Mo-free C40 $\text{Ti}(\text{Si}_{1-x}\text{Ge}_x)_2$ precursors grown by pulsed KrF laser annealing at 0.3 J/cm^2 for 50 pulses.

microstructures were observed by plan-view transmission electron microscopy (TEM) and cross-sectional TEM (XTEM). The depth profiles of the chemical species in the films were analyzed by energy dispersive spectrometry (EDS), which was equipped with a field-emission gun with an electron probe 1.2 nm in size. Grazing incidence x-ray diffraction (XRD) was carried out for phase identification with the incident angle fixed at 0.5° .

For the $\text{Ti}/\text{Si}_{0.76}\text{Ge}_{0.24}$ samples annealed by a pulsed KrF laser at an energy density of $0.2\text{--}0.3 \text{ J/cm}^2$ for $30\text{--}50$ pulses, Mo-free C40 $\text{Ti}(\text{Si}_{1-x}\text{Ge}_x)_2$ films were formed. Figure 1 shows the electron diffraction pattern (DP) of C40 $\text{Ti}(\text{Si}_{1-x}\text{Ge}_x)_2$, which is consistent with the XRD pattern of C40 $(\text{Ti}, \text{Mo})\text{Si}_2$.^{24,25} It is suggested that for pulsed-laser annealing the rapid melt/solidification process allows preferential growth of metastable C40 $\text{Ti}(\text{Si}_{1-x}\text{Ge}_x)_2$ requiring lower activation energy. Upon subsequent rapid thermal annealing at 650°C for 30 s, the metastable C40 phase was transformed to the C49 phase. The C54 phase was not formed until the annealing temperature reached 750°C . This result revealed that upon rapid thermal annealing the Mo-free C40 precursors could not be directly transformed to the C54 phase without going through the C49 phase. For the C40 and C54 TiSi_2 , their hexagonal planes stack in the *ABCABC* and *ABCDABCD* orders, respectively. The two stacking patterns are very similar to each other. Therefore, it has been suggested that the C40 phase may provide a crystallographic template for nucleation of the C54 phase,^{7-9,12} resulting in a lower C49-C54 transformation temperature. However, the present results seem to indicate that in addition to the structure or kinetics effect, other effects may also be responsible for the enhanced formation of the C54 phase.

Figure 2 shows the initial formation temperature of the C54 $(\text{Ti}, \text{Mo})(\text{Si}_{1-x}\text{Ge}_x)_2$ as a function of the thickness of the interposed Mo layer. With increasing the Mo thickness, the C54 formation temperature first decreases from 750°C to 600°C and then increases up to 650°C . In the present study, the C54 formation temperature was determined by analyzing the DP of the annealed sample. It should be noted that below the C54 formation temperatures, ranging from 600 to 650°C , the C40 phase was formed instead of the C49 phase. With

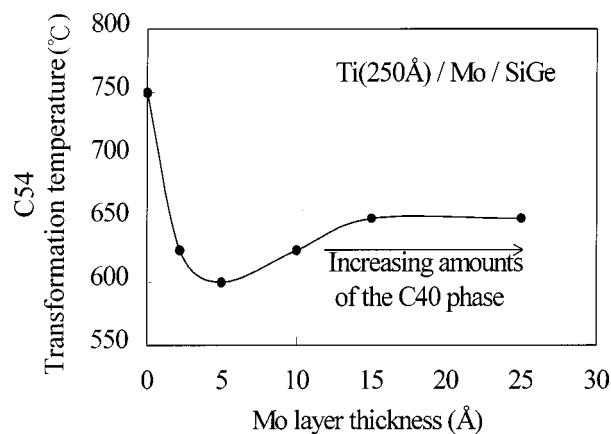


FIG. 2. Initial formation temperature of the C54 phase as a function of the thickness of the interposed Mo layer.

increasing the annealing temperature the amounts of the C54 phase increased, as shown in Fig. 3. For the $\text{Ti}(25 \text{ nm})/\text{Mo}(0.5 \text{ nm})/\text{Si}_{0.76}\text{Ge}_{0.24}$ samples annealed at 600°C , the EDS/XTEM analysis showed that significant amounts of Ti remained in the film surface and most of the Mo was still concentrated around the interface of $\text{Ti}/\text{Si}_{0.76}\text{Ge}_{0.24}$, where the Mo concentration was about 6 at.%, as shown in Fig. 4. Between the remaining Ti layer and the $\text{Si}_{0.76}\text{Ge}_{0.24}$ film the C40 phase was formed concurrently with a trace amount of the C54 phase. Upon annealing at 700°C Ti was completely consumed and the C54 phase became dominant, meanwhile the distribution of Mo became more homogeneous, the average Mo concentration being in the range of $1.0\text{--}2.5$ at.%. These results indicate that a relatively low Mo concentration in the $(\text{Ti}, \text{Mo})(\text{Si}_{1-x}\text{Ge}_x)_2$ layer promotes the formation of the C54 phase.

For the $\text{Ti}/\text{Mo}/\text{Si}_{0.76}\text{Ge}_{0.24}$ samples annealed at a temperature of $600\text{--}700^\circ\text{C}$, the amounts of the C40 phase increased with the thickness of the interposed Mo layer. This result is similar to the previous report that the amounts of the C40 phase increase with the Ta or Nb concentration in the Ti alloy.¹² For the samples with the interposed Mo layer 2.5 nm thick, the C40 phase was still dominant even after annealing

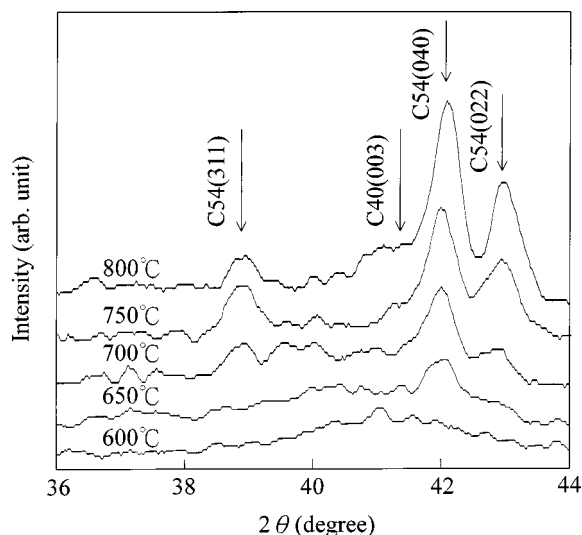


FIG. 3. XRD patterns of the $\text{Ti}(25 \text{ nm})/\text{Mo}(0.5 \text{ nm})/\text{Si}_{0.76}\text{Ge}_{0.24}$ samples annealed at various temperatures.

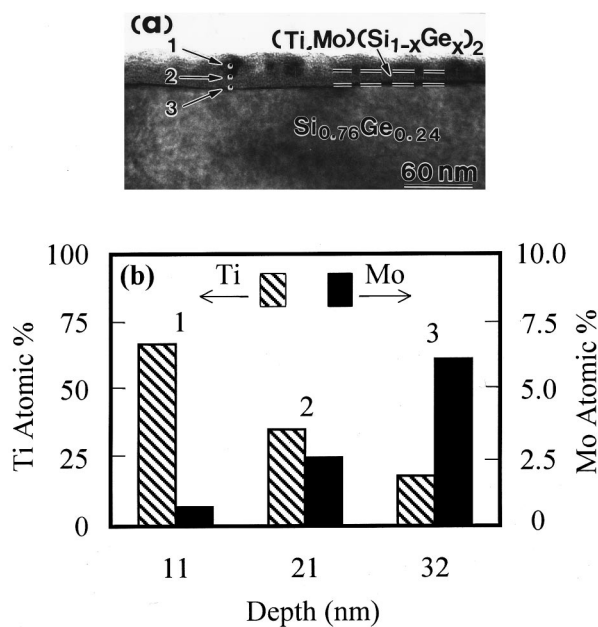


FIG. 4. (a) XTEM image and (b) depth profiles of Ti and Mo for a Ti(25 nm)/Mo(0.5 nm)/Si_{0.76}Ge_{0.24} sample annealed at 600 °C for 30 s.

at 700 °C. Besides, from EDS/XTEM analysis the Mo concentration of the (Ti, Mo)(Si_{1-x}Ge_x)₂ layer was in the range of 8–19 at. %. These results confirm that a relatively high Mo concentration in the (Ti, Mo)(Si_{1-x}Ge_x)₂ layer favors the formation of the C40 phase.

The formation temperature of C54 TiSi₂ can be increased by replacing Si with electron acceptors such as Al,¹⁵ or decreased by replacing Ti with electron donors such as refractory metals.^{6–12} It has been proposed that the stable TiSi₂ phase evolves from C49 to C54 and then to C40 with increasing the electron/atom ratio.¹⁶ In the present study, the Mo-free C40 phase grown by pulsed-laser annealing was transformed to C49 at 650 °C and then to C54 at 750 °C, revealing that upon rapid thermal annealing the Mo-free C40 phase was unstable and could not act as a template to nucleate the C54 phase. Even so, it should be noted that for the stable C40 phase, e.g., C40 (Ti, Mo)(Si_{1-x}Ge_x)₂, the possibility for the template mechanism cannot be ruled out. For the Ti/Mo/Si_{0.76}Ge_{0.24} samples annealed at a temperature of 575–800 °C, the C40 phase was first formed at lower temperatures and then transformed to C54 at higher temperatures, no C49 was observed. Meanwhile, the EDS/XTEM analysis showed that the Mo concentration in the reacted region was higher for lower-temperature annealing than for higher-temperature annealing. These data indicate that with increasing the Mo concentration in the reacted region, the phase stability shifts from C54 to C40 and no C49 is present. As a consequence, the electron/atom ratio as well as the C40 template mechanism may play important roles in the enhanced formation of the C54 phase.

In summary, upon rapid thermal annealing the Mo-free C40 Ti(Si_{1-x}Ge_x)₂ phase could not be directly transformed to the C54 phase without going through the C49 phase. For the Ti/Mo/Si_{0.76}Ge_{0.24} system the initial formation temperature of the C54 phase was shown to be a function of the

thickness of the interposed Mo layer. Upon annealing at a minimum temperature of 600 °C, the C54 phase was noted to be formed in the samples having an interposed Mo layer with a thickness of 0.5 nm. With increasing the Mo concentration in the reacted region the phase stability shifted from C54 to C40 and no C49 was observed. It seems that for the Ti/Si_{1-x}Ge_x system with an interposed Mo layer, apart from the C40 template mechanism, the electron/atom ratio is also responsible for the enhanced formation of the C54 phase.

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- ²⁵Standard JCPDS diffraction pattern 7-331 [hexagonal (Ti_{0.8}Mo_{0.2})Si₂], JCPDS-International Center for Diffraction Data, PDF-2 Database, Newton Square, PA.