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Effects of an interposed Mo layer on the interfacial reactions of Ti/$Si_{0.76}Ge_{0.24}$ by rapid thermal annealing and pulsed laser annealing

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Abstract. The thickness effect of an interposed Mo layer between Ti and $Si_{0.76}Ge_{0.24}$ films on the lowering of the formation temperature of C54 (Ti, Mo)$(Si_{1-x}Ge_x)_2$, thereby reducing Ge segregation and agglomeration of the C54 (Ti, Mo)$(Si_{1-x}Ge_x)_2$ films, is studied. Upon rapid thermal annealing, the interposed Mo layer can significantly reduce the formation temperature of C54 (Ti, Mo)$(Si_{1-x}Ge_x)_2$; however, the amount of reduction decreases with the Mo thickness. The electron/atom ratio seems to be one of the important factors in the lowering of the formation temperature of C54 (Ti, Mo)$(Si_{1-x}Ge_x)_2$. For the samples having an interposed Mo layer 0.5 nm thick a smooth C54 (Ti, Mo)$(Si_{1-x}Ge_x)_2$ film without Ge segregation can be grown after annealing at a temperature of 625–650 °C. For pulsed KrF laser annealing the rapid melt/solidification process allows only growth of C40 Ti$(Si_{1-x}Ge_x)_2$ or C40 (Ti, Mo)$(Si_{1-x}Ge_x)_2$ even though an interposed Mo layer is introduced into the Ti/$Si_{0.76}Ge_{0.24}$ samples, indicating that upon pulsed laser annealing the kinetic effect can dominate over the thermodynamic effect.

1. Introduction

$TiSi_2$ 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 (base-centred orthorhombic) or as the low-resistivity C54 phase (face-centred orthorhombic) [1]. For device applications the C54 $TiSi_2$ is preferred because of its lower resistivity. The C49 $TiSi_2$ generally forms first at temperatures ranging from 550 to 700 °C and then transforms to the C54 $TiSi_2$ at temperatures above 750 °C. As the lateral dimension of silicide features is decreased to the submicron regime the formation temperature of the C54 $TiSi_2$ substantially increases due to a lack of the C54 nuclei [2]. This phenomenon is sometimes referred to as the ‘fine-line effect’. The morphological stability of the C54 phase during high-temperature annealing is crucial to the development of ULSI technology.

$Si_{1-x}Ge_x$ material offers the promises of greater carrier mobility with respect to Si and bandgap engineering, and hence has potential applications in high-speed electronic and optoelectronic devices [3]. Therefore, the motivation for studying the Ti/Si system is favourably transferred to the Ti/$Si_{1-x}Ge_x$ system [4–9]. However, Ge segregation is generally regarded to occur after high-temperature annealing, which renders the morphological stability of C54 Ti$(Si_{1-x}Ge_x)_2$ more serious than that of C54 $TiSi_2$. It is likely that reducing the C54 transformation temperature would improve the morphological stability of C54 Ti$(Si_{1-x}Ge_x)_2$.

Recently, it has been shown that the C49–C54 transformation temperature can be lowered by preamorphization of Si substrates before Ti deposition [10–12], ion implantation of Mo or W into Si substrates before Ti deposition [13, 14] and deposition of an interposed layer of refractory metals or alloys between the Ti film and Si substrate, respectively [15–19]. 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 grain junctions in the C49 phase [12, 17, 20]. It has been reported that the C54 phase preferably nucleates at triple grain junctions of the C49 phase, where the energy barrier for nucleation of the C54 phase can be significantly reduced [20]. The enhanced growth of the C54 phase by the interposition of a refractory

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metal layer may be ascribed to the formation of the C40 template [14, 16, 19] or the electron/atom ratio [21, 22]. Hume-Rothery [23] pointed out that the structure of some intermediate phases is dependent on the electron/atom ratio, where the number of electrons is taken as the group number in the periodic table, except that the number of electrons assigned to the transition elements, group VIII, is zero. Gouldshmidt [24] observed that the structure of refractory silicides from $TiSi_2$ to WSi_2 and their alloys is also sensitive to the electron/atom ratio.

In the present study, an Mo layer is interposed in the $Ti/Si_{0.76}Ge_{0.24}$ system to study its thickness effect on the lowering of the C54 transformation temperature. From this result, the adequate conditions used for growing a smooth C54 $(Ti, Mo)(Si_{0.76}Ge_{0.24})_2$ film without Ge segregation are explored. In addition, the interfacial reactions of $Ti/Si_{0.76}Ge_{0.24}$ and Ti/Mo (0.5 nm)/$Si_{0.76}Ge_{0.24}$ by pulsed KrF laser annealing are also discussed.

2. Experimental procedures

$Si_{0.76}Ge_{0.24}$ films with thicknesses of 100 and 150 nm, respectively, were grown at 550 °C in an ultrahigh-vacuum chemical vapour deposition system. Ti films about 25 nm thick were deposited onto the $Si_{0.76}Ge_{0.24}$ films at a rate of 0.1 nm s^{-1} in an electron gun deposition system. The base pressure was about 1.0×10^{-6} 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 4×4 mm^2. Phase formation and 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 analysed by an energy dispersive spectrometer (EDS) on the TEM equipped with a field emission gun with an electron probe 1.2 nm in size. Grazing incidence x-ray diffraction (GIXRD) was carried out with the incident angle fixed at 0.5° for phase identification. The sheet resistance of the annealed samples was measured by the four-point probe method.

3. Results and discussion

3.1. $Ti/Si_{0.76}Ge_{0.24}$

For the samples annealed at 650 °C $Ti(Si_{1-x}Ge_x)_2$ was formed, while it was transformed to C54 $Ti(Si_{1-x}Ge_x)_2$ at 750 °C concurrently with the appearance of agglomeration as shown in figure 1, in which the discrete C54 $Ti(Si_{1-x}Ge_x)_2$ islands are observed. From EDS/XTEM analysis, the C54 $Ti(Si_{1-x}Ge_x)_2$ grains are Ge deficient, while the $Si_{1-x}Ge_x$ between the C54 $Ti(Si_{1-x}Ge_x)_2$ grains is Ge rich. During high-temperature annealing Ge diffuses from the C54 $Ti(Si_{1-x}Ge_x)_2$ grains into the C54 $Ti(Si_{1-x}Ge_x)_2$ grain boundaries to react with Si and Ge from the substrate, forming Ge-rich $Si_{1-x}Ge_x$ [6]. That Ti preferably reacts with Si may be ascribed to the larger heat of formation for $TiSi_2$, −55 kJ $mole^{-1}$, than for $TiGe_2$, −47 kJ $mole^{-1}$ [25].

In our previous studies [26–28], pulsed KrF laser annealing had been shown to be an effective method to grow smooth germanosilicide films without Ge segregation and agglomeration. In this work, pure Ti germanosilicide films can be grown at an energy density of 0.1–0.3 J cm^{-2} for 30–50 pulses. Outside these annealing conditions constitutional supercooling and amorphous structures readily occur. As seen in figure 2 the electron diffraction pattern (DP) of Ti germanosilicide was identified to be that of C40 $Ti(Si_{1-x}Ge_x)_2$, which is consistent with the XRD pattern of C40 (Ti, Mo)Si_2†‡. No C49 or C54 $Ti(Si_{1-x}Ge_x)_2$ were observed. Upon subsequent rapid thermal annealing the metastable C40 $Ti(Si_{1-x}Ge_x)_2$ was transformed to C49 and C54 $Ti(Si_{1-x}Ge_x)_2$ at 650 and 750 °C, respectively. For C40 and C54 (Ti, Mo)Si_2, the hexagonal planes stack in the ABCABC and ABCDABCD orders, respectively. It has been reported that the structural similarity and close lattice mismatch between C40 and C54 (Ti, Mo)Si_2 render C40 (Ti, Mo)Si_2 to act as a template to nucleate C54 (Ti, Mo)Si_2, giving rise to the reduction of the C54 transformation temperature [14–16, 19]. In contrast, the present study shows that upon annealing the Mo-free C40 $Ti(Si_{1-x}Ge_x)_2$ precursors cannot be directly transformed to C54 $Ti(Si_{1-x}Ge_x)_2$ without going through C49 $Ti(Si_{1-x}Ge_x)_2$. In C40 and C54 $(Ti, Mo)(Si_{1-x}Ge_x)_2$ some Ti are replaced with electron donors such as Mo. As a consequence, in addition to the template mechanism the electron/atom ratio also plays an important role in the enhanced formation of the C54 phase [21, 22, 29].

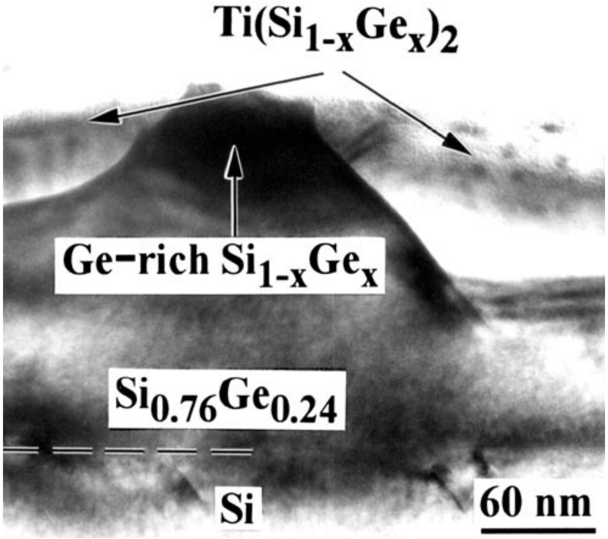

Figure 1. TEM image of the $Ti/Si_{0.76}Ge_{0.24}$ sample annealed at 750 °C showing agglomeration.

3.2. $Ti/Mo/Si_{0.76}Ge_{0.24}$

The sheet resistance of Ti germanosilicide films as a function of the annealing temperature and Mo thickness is shown in figure 3. The resistivity of C49 $TiSi_2$ is in the range of

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† Standard JCPDS diffraction pattern 6-607 (hexagonal $(Ti_{0.4}Mo_{0.6})Si_2$), JCPDS-International Center for Diffraction Data, PDF-2 Database, Newton Square, PA, USA.

‡ Standard JCPDS diffraction pattern 7-331 (hexagonal $(Ti_{0.8}Mo_{0.2})Si_2$), JCPDS-International Center for Diffraction Data, PDF-2 Database, Newton Square, PA, USA.

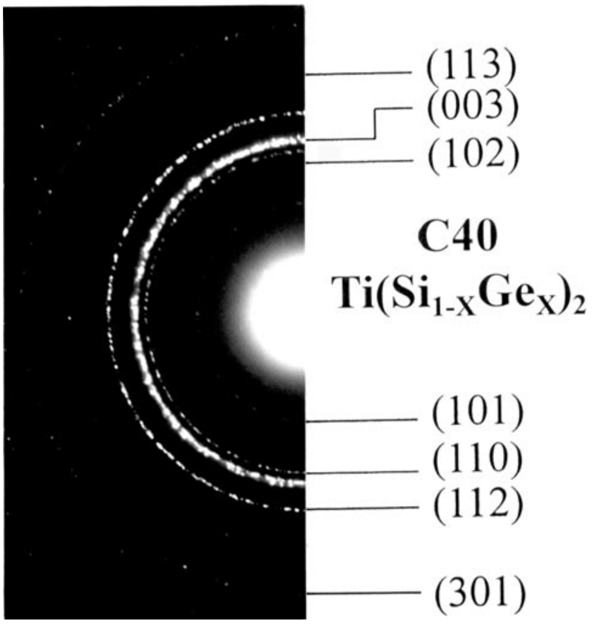

Figure 2. Electron DP of the Mo-free C40 $Ti(Si_{1-x}Ge_x)_2$ precursors grown by pulsed KrF laser annealing at 0.3 J cm^{-2} for 50 pulses.

60–70 $\mu\Omega$ cm, while that of C54 $TiSi_2$ is in the range of 15–20 $\mu\Omega$ cm. Therefore, a sharp drop in sheet resistance in figure 3 reveals the formation of appreciable C54 (Ti, Mo)$(Si_{1-x}Ge_x)_2$. Similar results have been reported [18, 19, 21]. As seen in figure 3 an interposed Mo layer significantly reduces the formation temperature of C54 (Ti, Mo)$(Si_{1-x}Ge_x)_2$, and the amount of reduction decreases with increasing Mo thickness. This result is consistent with the XRD analysis of the Ti germanosilicide films formed at 650 °C. Upon annealing at 650 °C C54 (Ti, Mo)$(Si_{1-x}Ge_x)_2$ is dominant in the samples having a Mo thickness of 0.5–1.0 nm, while it is not apparently observed in the samples having a Mo thickness of 1.5–2.5 nm. Correspondingly, TEM observation revealed that the amount of C40 (Ti, Mo)$(Si_{1-x}Ge_x)_2$ increased with the Mo thickness. Although the amounts of C54 (Ti, Mo)$(Si_{1-x}Ge_x)_2$ increased with the annealing temperature, C40 (Ti, Mo)$(Si_{1-x}Ge_x)_2$ was still dominant even after annealing at 700 °C for the samples having an interposed Mo layer 2.5 nm thick. These results reveal that in order to grow significant amounts of C54 (Ti, Mo)$(Si_{1-x}Ge_x)_2$ at lower temperatures the thickness of the interposed Mo layer should be less than 1.0 nm.

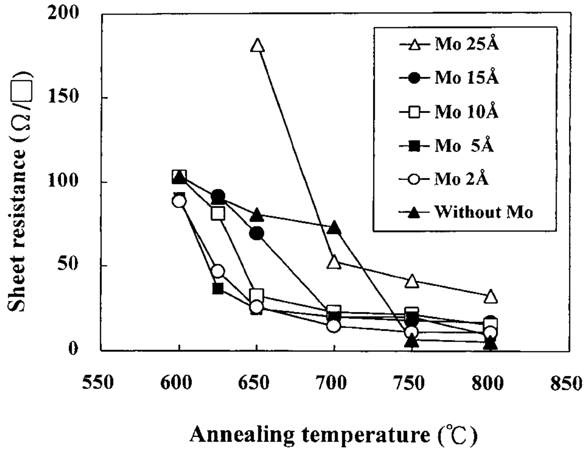

Figure 3. Sheet resistance of the Ti/Mo/$Si_{0.76}Ge_{0.24}$ samples versus the annealing temperature as a function of the thickness of the interposed Mo layer.

As shown in figure 3 the sheet resistance of the Ti germanosilicide films is dramatically reduced at 625 °C for the samples having a Mo thickness of 0.5 nm. Correspondingly, TEM examination also revealed that significant amounts of C54 (Ti, Mo)$(Si_{0.76}Ge_{0.24})_2$ were formed after annealing at 625 °C as seen in figure 4. Therefore, it is likely that the growth of a smooth C54 (Ti, Mo)$(Si_{0.76}Ge_{0.24})_2$ film without Ge segregation could be achieved for the Ti/Mo (0.5 nm)/$Si_{0.76}Ge_{0.24}$ samples after annealing at a low temperature. Actually, for the Ti/Mo (0.5 nm)/$Si_{0.76}Ge_{0.24}$ samples annealed at a temperature of 625–650 °C agglomeration and Ge segregation to the unreacted $Si_{0.76}Ge_{0.24}$ were effectively suppressed as shown in figure 5. Above 700 °C, however, Ge segregation apparently appeared. Nevertheless, the present results show that for the Ti/Mo/$Si_{0.76}Ge_{0.24}$ system the interposed Mo layer with an adequate thickness can significantly reduce the C54 transformation temperature and thereby effectively suppress the agglomeration and Ge segregation of the C54 (Ti, Mo)$(Si_{0.76}Ge_{0.24})_2$ films.

Some Ti/Mo (0.5 nm)/$Si_{0.76}Ge_{0.24}$ samples were also annealed by a pulsed KrF laser at an energy density of 0.1–0.5 J cm^{-2} for 50 pulses. It is interesting that only C40 (Ti, Mo)$(Si_{1-x}Ge_x)_2$ was observed. The introduction of an interposed Mo layer into Ti/$Si_{0.76}Ge_{0.24}$ samples seems not to enhance the formation of C54 (Ti, Mo)$(Si_{1-x}Ge_x)_2$. The aforementioned results of the Ti/$Si_{0.76}Ge_{0.24}$ system have also shown that pulsed KrF laser annealing only grows the C40 $Ti(Si_{1-x}Ge_x)_2$ phase. It is suggested that for pulsed laser annealing the rapid melt/solidification process allows only growth of C40 $Ti(Si_{1-x}Ge_x)_2$ or C40 (Ti, Mo)$(Si_{1-x}Ge_x)_2$ requiring lower activation energy, indicating that in these interfacial reactions the effect of rapid melt/solidification process (kinetics effect) is dominant over that of the electron/atom ratio (thermodynamic effect).

4. Summary and conclusions

(a) An interposed Mo layer between Ti and $Si_{0.76}Ge_{0.24}$ can significantly reduce the formation temperature of C54 (Ti, Mo)$(Si_{1-x}Ge_x)_2$ with the amount of reduction decreasing with the Mo thickness. Both the electron/atom ratio and the template mechanism seem to have important effects on the lowering of the formation temperature of C54 (Ti, Mo)$(Si_{1-x}Ge_x)_2$.

(b) For the Ti/Mo (0.5 nm)/$Si_{0.76}Ge_{0.24}$ samples annealed at a temperature of 625–650 °C, a smooth C54 (Ti, Mo)$(Si_{0.76}Ge_{0.24})_2$ film without Ge segregation can be grown.

(c) Pulsed KrF laser annealing allows only growth of C40 $Ti(Si_{1-x}Ge_x)_2$ or C40 (Ti, Mo)$(Si_{1-x}Ge_x)_2$ even though Mo is introduced into the Ti/$Si_{0.76}Ge_{0.24}$ system, revealing that in these interfacial reactions the kinetic effect is dominant over the thermodynamic effect.

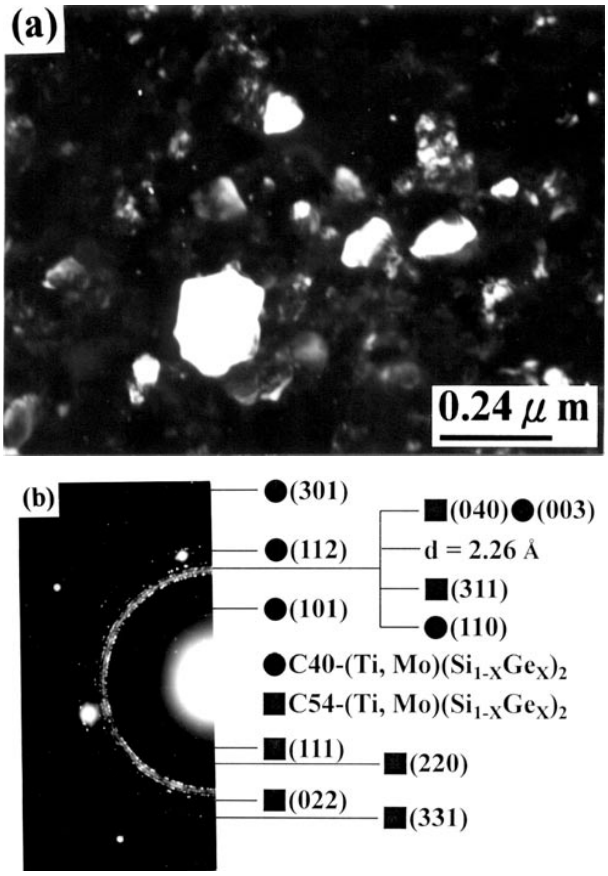

Figure 4. (*a*) Dark-field image taken with the (331) diffracted beam of C54 (Ti, Mo)$(Si_{1-x}Ge_x)_2$ and (*b*) DP for a Ti (25 nm)/Mo (0.5 nm)/$Si_{0.76}Ge_{0.24}$ sample annealed at 625 °C for 30 s showing the formation of appreciable C54 (Ti, Mo)$(Si_{1-x}Ge_x)_2$ grains.

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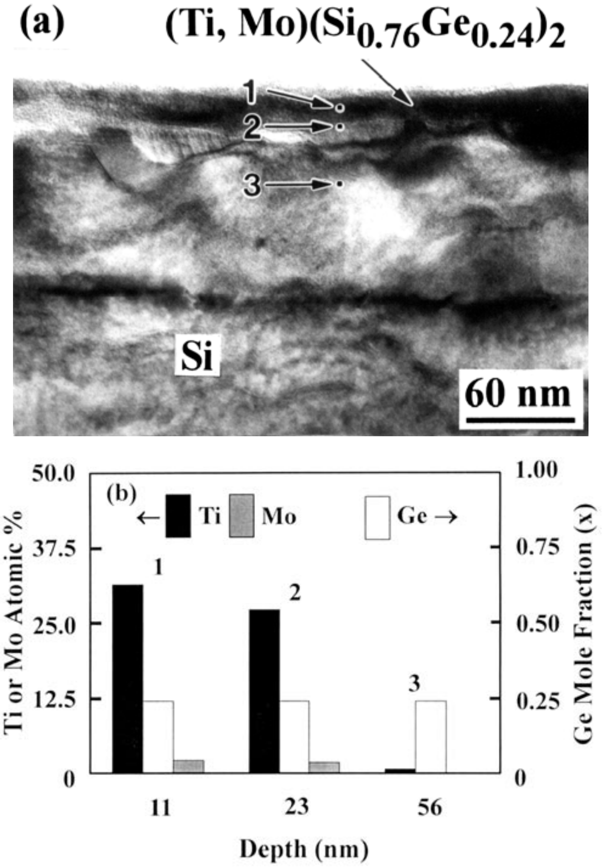

Figure 5. (*a*) XTEM image and (*b*) the depth profiles of Ti, Mo, and Ge for a Ti (25 nm)/Mo (0.5 nm)/$Si_{0.76}Ge_{0.24}$ sample annealed at 625 °C for 30 s.

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