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Silicide Formation from Laser Thermal Processing of Ti/Co Bilayers

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A bilayered CoTi silicide structure consisting of an amorphous CoTi silicide and a highly textured CoTi silicide was found after pulsed excimer laser annealing of titanium/cobalt/silicon stack at high fluence of 0.6 J/cm². The highly textured CoTi silicide is monocrystalline and fully coherent with the Si(111) plane of the substrate but has a large amount of microstructural defects. The constitutional supercooling phenomenon is the solidification mechanism responsible for the highly textured CoTi silicide. The incomplete crystallization shown by the presence of the amorphous CoTi silicide is attributed to a high concentration of titanium impurity.

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A new field of metal-silicon interactions has been established with the prevalent application of pulsed laser processing of semiconductor materials. The main feature of the reaction between metal and semiconductor under this transient condition compared to those under steady-state condition is the product of metastable reaction.^{1,2} When a nanosecond, high-power laser pulse is irradiated on a binary system, a rapid surface melting and solidification with a fast cooling rate in the order of $\sim 10^{10}$ K/s takes place. During the solidification, metastable crystalline, and/or amorphous alloys are formed depending on the magnitude of the liquid-solid interfacial velocity.^{1,3,4} In this paper, we present the preliminary results of single pulsed excimer laser-induced reactions of Ti-capped cobalt with silicon.

Experimental

The starting material was a p-type silicon (100) wafer. A diluted hydrofluoric acid etch was carried out prior to a metal deposition to remove any native oxide on the blanket wafer. A 12 nm Co was deposited, followed by the deposition of a 12.5 nm Ti using *in situ* dc magnetron sputtering. The Ti cap is supposed to protect cobalt during laser annealing as cobalt is vulnerable to oxygen.⁵ The samples were then irradiated in normal ambient (class 100 clean room) with a 248 nm KrF laser. Only one pulse with pulse duration of 23 ns was used. Grazing incidence X-ray diffraction (XRD, $\theta = 1^\circ$) and micro-Raman spectroscopy technique were used for phase identification. Auger electron spectroscopy (AES) was used to investigate the depth profile of silicide after laser thermal annealing. Cross-sectional transmission electron microscopy (XTEM) was used to study the silicide layer morphology. Electron dispersive X-ray spectroscopy (EDS) and electron energy loss spectroscopy (EELS) techniques in TEM were used to determine the localized elemental composition.

Results and Discussion

Figure 1 shows the XRD spectra of a Ti/Co/Si sample after a single pulse laser irradiation at 0.6 J/cm². As compared to a rapid thermal annealed sample, a diffraction peak at 28.9° corresponding to CoSi₂(111) phase can be identified. Micro-Raman spectra (not shown here) confirmed that there were no frequency shifts at 204, 220, and 150 cm⁻¹ for the pulsed laser annealed samples,⁶ further indicating the absence of CoSi and Co₂Si phases.

Figure 2 shows the AES depth profiles of a Ti/Co/Si sample before and after a 0.6 J/cm² laser annealing. Note that a TiO_x layer remains intact on the surface of Ti/Co/Si sample before and after annealing. The rapid heating by the single pulsed laser annealing

had little effect on the depth profile of TiO_x, implying insignificant diffusion of oxygen atoms during the laser annealing process. The Ti atoms beneath the TiO_x layer diffused toward the Si substrate and intermixed with Co and Si, leading to the formation of CoTi silicide.

Figure 3 shows the XTEM obtained from the Ti/Co/Si sample of which the XRD spectra are shown in Fig. 1. The top layer of ~ 5 nm is an amorphous TiO_x, confirming the TiO_x results seen in Fig. 2. The middle layer of ~ 72 nm is an amorphous CoTi silicide with a uniform surface and the bottom layer (~ 23 nm) is a CoTi silicide that is highly orientated to the (111) direction of the Si substrate. The EDS and Auger analysis of the amorphous CoTi silicide layer show that the ratio of Co:Ti:Si near the surface and immediately above the textured layer is 23:40:37 and 33:12:55, respectively. Whereas, the ratio of Co:Ti:Si in the textured CoTi silicide layer is about 14:4:82. Figure 4 shows a HRTEM image of the highly textured CoTi(111) silicide//Si(111) system on the Si(100) substrate. The favorable growth of the CoTi silicide along the (111) plane is due to its lowest interface energy with the Si(111) plane.⁷ Crystalline defects resembled branches and stems appearing as dark contrast (see Fig. 4) correspond to cobalt-rich region (relative to titanium) revealed by an EELS Co elemental mapping as shown in Fig. 5.

The possible growth mechanism for the formation of the microstructure in Fig. 3 is as follows. When a single pulse laser of 0.6

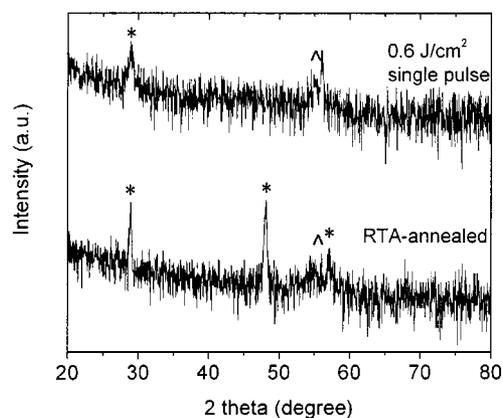


Figure 1. Grazing incidence XRD spectra of a Ti/Co/Si sample annealed with single pulse excimer laser at 0.6 J/cm². A RTA-annealed sample is included for comparison. The RTA experiments were performed using a two-step RTA at 450 and 825°C for 30 s in a N₂ ambient. The XRD peaks indicated as (*) and (λ) correspond to CoSi₂ and Si, respectively.

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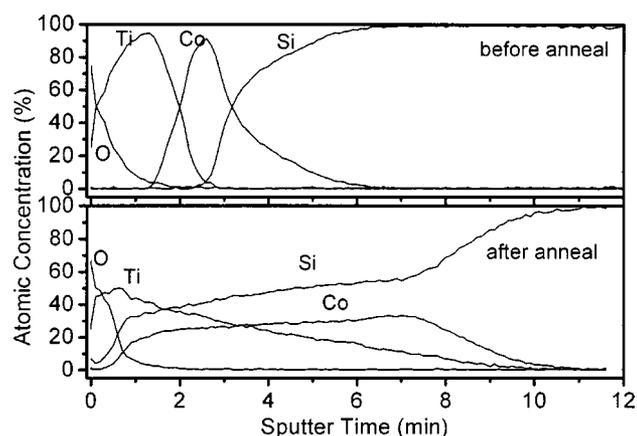


Figure 2. AES depth profiles of a Ti/Co/Si sample before annealing and after annealing with a single laser pulse at 0.6 J/cm^2 .

J/cm^2 is irradiated on the surface of a Ti/Co/Si stack, the energy of the laser pulse is high enough to cause melting of Ti, Co, and Si. As can be seen from Fig. 3, the melt front has propagated down to $\sim 100 \text{ nm}$ of depth. In the initial molten state, the Ti/Co metal layers and the Si substrate undergo a mixing via liquid phase diffusion.⁴ As a result, a variation in the composition of the Co and Ti resulted in the liquid phase. When the melt front reaches the substrate during the laser irradiation, the single crystalline Si substrate which acts as a seed for the epitaxial regrowth, facilitates the nucleation in an epitaxial manner during solidification. The growth kinetic is based upon liquid-phase epitaxy regrowth.^{4,8} The rapid quenching rate of the melt resulted in a large amount of supercooling, and this gives rise to a driving force for a solidification accompanied by a decrease in the free energy of the system. During solidification, the (111) plane of the CoTi silicide tends to grow along the Si(111) substrate due to its lowest interface energy. As the solidification front proceeds further into the molten liquid, due to the presence of a high concentration of titanium impurity ($\sim 12\%$ as shown in Fig. 2 and 3), a change in the thermodynamics has possibly led to a transition from the textured CoTi silicide to an amorphous CoTi silicide similar to the phenomenon suggested by Gong *et al.*⁹ for the solidification transition from a crystalline to an amorphous phase. The presence of titanium atoms has modified the solidification temperature and growth dynamics.¹⁰ This is possible because there is a large negative heat of mixing associated with the presence of a large

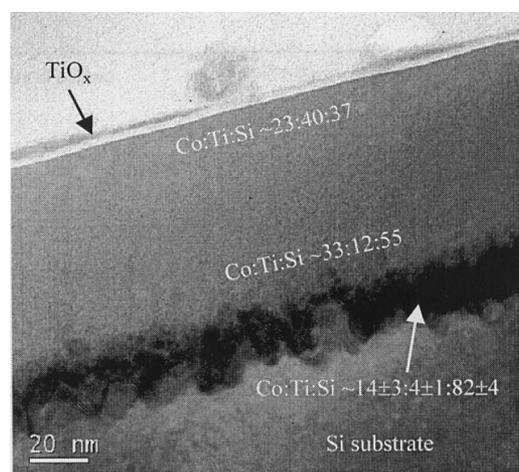


Figure 3. XTEM of the Ti/Co/Si sample after pulsed laser irradiation at 0.6 J/cm^2 shown in Fig. 1. A bilayered structure, *i.e.*, an amorphous CoTi silicide layer on a highly textured CoTi silicide layer, can be seen.

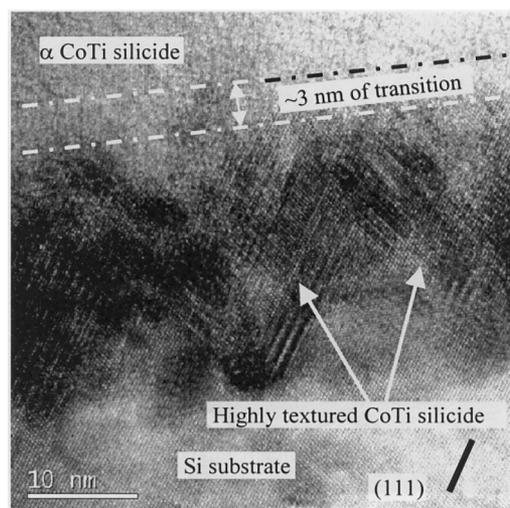


Figure 4. HRTEM image of a portion of the highly textured CoTi silicide layer shown in Fig. 3. The textured CoTi silicide grows along the (111) direction of the silicon substrate.

quantity of the titanium impurities in the composition range as detected by the Auger and EDS analysis data shown in Fig. 2 and 3, respectively. To confirm the effect of the Ti cap on pulsed laser annealing, a single pulsed laser annealing on pure Co on Si substrate without any Ti cap at a similar fluence was performed. Only a layer of polycrystalline Co silicide (*i.e.*, without the presence of any amorphous phase) was observed. The formation of the amorphous CoTi silicide also can result from the supercooled/undercooled liquid in which its temperature has fallen below the melting temperature of the CoTi silicide amorphous phase.^{11,12} As a result of the supercooled liquid, the velocity of the solidifying interface has exceeded the estimated value of 1.5 m/s .⁸ With this fast solidification velocity, the amorphous CoTi silicide layer propagates upward until it reaches the surface.

Figure 6 shows the TEM planar view of a pulsed laser-annealed Ti/Co/Si stack. Cellular structures which are typical consequences of constitutional supercooling (CSC)^{1,13,14} can be seen. The presence of the CSC phenomenon is due to the actual temperature in the CoTi silicide liquid near the solid-liquid interface is less than that of the

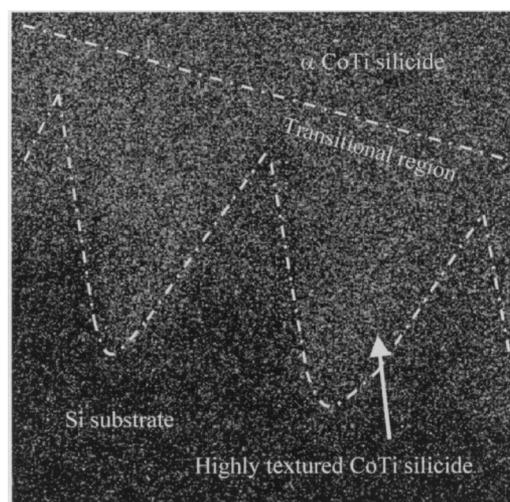


Figure 5. Elemental mapping of Co of a section of the highly textured CoTi silicide layer. The brighter contrast in the elemental map corresponds to cobalt-rich region.

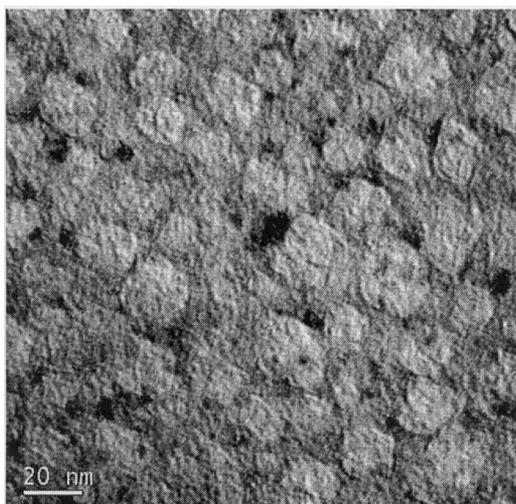


Figure 6. Planar view TEM of a Ti/Co/Si sample annealed at 0.6 J/cm². Formation of cellular structures after laser irradiation can be clearly seen.

liquidus temperature. In addition, due to the presence of a compositional gradient of solute atoms (*i.e.*, cobalt and titanium) as a function of depth in the melt, CSC takes place along with segregation of solute atoms during solidification. Because the solubility of the cobalt and titanium atoms in solid Si is much less than that in liquid Si, the solute atoms are rejected from the solid during the solidification in the supercooled liquid ahead of the interface. This results in a lower Co concentration detected in the textured CoTi silicide than that near the interface of the amorphous CoTi silicide and the highly textured CoTi silicide (Fig. 3). In addition there is an obvious increment in the Co concentration between the 7.5 and 10 min of the sputtering time in Fig. 2. Compared to the cobalt elemental mapping in Fig. 5, the dark contrasts shown by the textured layer in the HRTEM lattice image in Fig. 4, which resemble branches and stems extending upward in the (100) and outward in the (111) direction are cobalt-rich CoTi silicide. The presence of the segregation of solute atoms (see Fig. 4 and 5) contributed to the growth of the defect-occupied CoTi silicide grains during solidification, and this supports the CSC phenomenon. A schematic of the textured CoTi silicide with a high concentration of crystalline defects is illustrated in Fig. 7. A transitional layer of about ~3 nm (see Fig. 4) is suspected to be the mechanism responsible for the “milky” contrast seen in the planar TEM in Fig. 6.

Conclusion

In summary, the laser-induced reactions of Ti/Co/Si film stacks by irradiation of single pulse excimer laser at 0.6 J/cm² has given rise to the formation of a bilayered structure; a metastable epitaxial CoTi silicide and an amorphous CoTi silicide. The lowest interface energy of the Si(111) plane has acted as a seed layer and prompted the growth of a (111) oriented CoTi silicide from the supercooled liquid, resulting in a highly textured CoTi(111) silicide//Si(111) structure initially. The growth of this layered structure is accompanied by segregation of solute atoms, leading to the formation of cellular structures that can be explained by the CSC phenomenon. Due to the presence of a large concentration of titanium impurities

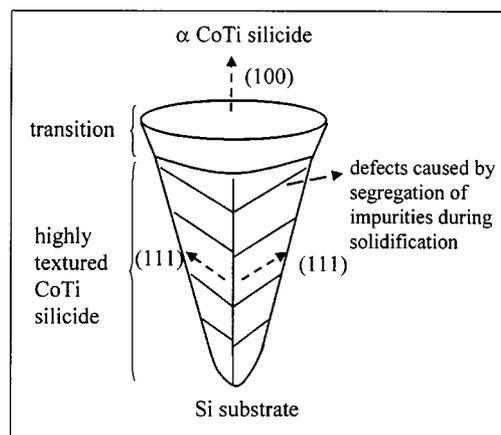


Figure 7. Schematic of the textured CoTi silicide showing defects due to segregation of cobalt impurities during CSC.

ahead of the textured crystallization layer (as shown in Fig. 2), the growth kinetics of the subsequent solidification front change, transforming the textured crystallization layer into an amorphous-like layer. In addition, the presence of a supercooled liquid just ahead of the solidification front of the textured layer may cause a fast quenching, resulting in a transition from the textured CoTi silicide to an amorphous CoTi silicide. The information is critical in the understanding of the formation of laser-annealed silicides for future Si device application.

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