Crystallinity of CoSi$_2$ nanolayer grown by refractory metal interlayer and cap layer methods

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Abstract. Epitaxial formation of CoSi$_2$ nanolayer by solid state reaction of Co-Si in refractory metal intermediate-layer and cap-layer systems was investigated. Thin films of Ta and W, as the refractory metal intermediate or cap layers of the Co film, were deposited on Si(100) substrate and then heat-treated. The both interlayers resulted in formation of epitaxial CoSi$_2$ with (100) crystallographic orientation at 900°C. However, in the Ta intermediated system, the grown CoSi$_2$ layer was thermally unstable at 1000°C, unlike the W system with a stable silicide layer. We found that use of W cap-layer cannot yield an epitaxial CoSi$_2$ phase. But, a Ta cap-layer resulted in formation of epitaxial CoSi$_2$(100) layer even in a lower temperature (800°C). Again, in the presence of Ta, the grown CoSi$_2$ layer was thermally unstable at 900°C.

1. Introduction

Based on the ITRS's report, typical dimensions of wires and contacts in nanoelectronics shrink down to 50 nm by 2010 [1]. Hence, there will be increasing demands for ultra shallow and uniform silicides in nanoscales. In this context, single-crystal epitaxial silicides are preferred over polycrystalline ones due to their smoother interfaces, superior thermal stability, and excellent layer uniformity. Among the most attractive silicides, CoSi$_2$ is preferable to TiSi$_2$ because of no scale effect on the resistivity [2]. Epitaxial growth on Si(100) substrates has shown to be far less straightforward than on Si(111) ones which are not widely used in the semiconductor technology. Therefore, modified methods have to be applied for preparing the epitaxial layers on Si(100) substrates [3,4,5].

In this work, we have studied and compared epitaxial formation of CoSi$_2$ nanolayer by solid state reaction of Co-Si in refractory metal intermediate-layer or cap-layer systems.

2. Experimental details

n-type Si(100) wafers with resistivity of 5-8 $\Omega$-cm were used as substrates. After a standard RCA cleaning procedure followed by dipping in a diluted HF solution, the substrates were loaded into a vacuum chamber (see some of the details in [6,7]). We have used a DC magnetron sputtering to deposit Ta or W layer with 10 nm in thickness. After the growth of the intermediate layer on the Si substrate, a Co layer with a thickness of about 15 nm was deposited using thermal evaporation method at a pressure of about 2.7$\times$10$^{-4}$ Pa (without breaking the vacuum), for producing Co/Ta/Si and Co/W/Si systems. For Ag/Ta/Co/Si and Ag/W/Co/Si systems, the Ag layer with 50 nm thickness was sputtered on the refractory layer/10 nm sputtered Co layer, without breaking the vacuum. During the deposition, a dynamic flow of ultrahigh purity Ar gas with pressure of 0.7 Pa was used for the sputtering discharge. Post annealing process of the films was performed in an N$_2$ ambient with a flow rate of 0.2 lit/min in a temperature range from 300 to 1000°C for 30 min. The electrical property of the annealed films was measured by four-point probe sheet resistance ($R_s$) technique, at room temperature. Phase formation and crystallographic orientation of the samples were determined by 0-20 X-ray diffractometry (XRD) from 20 to 80° with a step size of 0.005 using a Cu–K$_\alpha$ radiation source.

3. Results and discussion

Figure 1 shows $R_s$ values of the Co/Ta/Si and Co/W/Si systems annealed at different temperatures. By increasing the temperature, it is seen that there is a reduction in the $R_s$ value at 400°C relating to...
crystallization of the evaporated Co layer. The slight increase of $R_s$ value at 700 °C is due to simultaneous formation of both CoSi and CoSi$_2$ phases which is consistent with our XRD data. The $R_s$ value at 800 °C indicates complete formation of CoSi phase during formation of CoSi$_2$ layer at this temperature. The reduction of $R_s$ value to about 1 Ω□ at 900°C shows decomposition of CoSi phase and substantial formation of CoSi$_2$ layer, as inferred in [8]. For the Co/Ta/Si system, by increasing the temperature to 1000 °C, a rapid increase in the $R_s$ value was measured. This can be assigned to formation of Ta$_2$O$_5$ cap layer in the annealed Co/Ta/Si system and also decomposition of the formed CoSi$_2$ layer, as shown by our XRD analysis. Instead, the constant behavior of the $R_s$ value between 900 and 1000°C indicates thermal stability of the CoSi$_2$ layer in the Co/W/Si system. This observation is in agreement with our XRD analysis, too.

Figure 2 shows variation of $R_s$ measurement of the Ag/Ta/Co/Si and Ag/W/Co/Si multilayers at the different annealing temperatures. For the Ag/Ta/Co/Si system, no considerable change of $R_s$ value was observed up to 650°C meaning its thermal stability up to this high temperature. The slight increase of the $R_s$ value at 700°C shows interdiffusion of Ag/Ta layers while CoSi phase initiate to form. The reduction of the $R_s$ value at 750°C can be related to self-encapsulation of the Ta layer on the Ag layer and formation of CoSi$_2$, as both of them are in agreement with our RBS and XRD analyses, respectively. No substantial increase in the $R_s$ value at 800 and also 900°C is due to formation of Ag/CoSi$_2$ contact layer capped by the Ta layer. For the Ag/W/Co/Si system, again no considerable change of $R_s$ value was observed up to 500°C, although it shows a downward trend. This trend can be due to decrease of point defects and residual gases trapped in the sputtering process, being released during the heat-treatment [9]. By increasing the temperature to 600 and 650°C, the $R_s$ value showed a sharp increase (more than two orders of magnitude). AFM and RBS analyses (not shown here) indicated that the increase can be due to surface agglomeration of the Ag layer, and partially, due to interdiffusion of Ag/W layers [10]. The relatively high value of $R_s$ remained nearly constant at 700°C. However, at 750°C we observed a sudden reduction for the $R_s$ value which is related to CoSi$_2$ formation at Co/Si interface and/or self-encapsulation of the W layer on the Ag layer [10]. This low $R_s$ value (2 Ω□) remained constant up to 800°C. But, at 900°C, once again the $R_s$ value showed a sharp increase, due to complete mixing of the layers and also decomposition of the formed CoSi$_2$ phase, as observed by the XRD analysis.

Figure 3 illustrates XRD spectra of the Co/Ta/Si system annealed at different temperatures. At 550°C, the undiffused Co layer is crystallized and interdiffusion of Co and Ta atoms resulted in crystallization of Co$_2$Ta alloy phase at the Co/Ta interface which was also observed in some earlier works [11,12]. At 700°C, observation of CoSi and CoSi$_2$ peaks indicates initial reaction of the Co film with the Si substrate. The presence of Ta$_2$O$_5$ peaks means that the Ta layer reacted with the small amount of the residual oxygen in the environment. At 800°C, the initial phase of Co$_2$Ta completely
decomposed, and consequently, CoSi$_2$ phases appeared substantially. However, we have still a nearly poly-texture CoSi$_2$ layer along with some CoSi phase that is not consumed. Thus, by increasing the temperature to 900°C, the CoSi phase was consumed and we obtained strong diffraction peaks due to the series of (100) orientations for CoSi$_2$ phase which show an acceptable single crystalline growth of a CoSi$_2$ layer on the Si(100) substrate. Furthermore, formation of TaSi$_2$ was initiated at this temperature. But at 1000°C, a substantial amount of Co$_2$Ta phase reappeared and the CoSi$_2$ phase is also observed in a poly-texture form. Moreover, Ta reaction with nitrogen and residual oxygen of the ambient produced TaN and Ta$_2$O$_5$ phases at this temperature.

XRD spectra of the Co/W/Si system at the different annealing temperatures (not shown here) is relatively similar to the spectra of the Ta system [7]. At 550°C, a relatively intense Co peak appeared indicating the crystallization of Co layer without any solid state reaction at this temperature. At 700°C, CoSi phase was formed and a few Co$_2$Si peaks are also observed. At 800°C, the Co$_2$Si phase is almost fully converted to CoSi, and production of WSi$_2$ phase was initiated. In addition, the observed CoSi$_2$ peaks indicate transformation of CoSi phase to CoSi$_2$. At 900°C, CoSi phase is fully transferred to CoSi$_2$ with strong (100) orientations, indicating its epitaxial formation. By further increasing the temperature to 1000°C, no significant change of phase formation was observed meaning thermal stability of the formed CoSi$_2$ layer.

XRD spectra of the heat-treated Ag/Ta/Co/Si(100) multilayer has been shown in Figure 4. At 500°C, the Ag(111) peak is mainly observed without any phase formation. This crystallography characteristic was also dominant up to 650°C. At 700°C, the CoSi$_2$ phase formation with (400) orientation was initiated. By increasing the temperature to 800°C, the CoSi$_2$ formation and crystallization of the Ag layer was also increased. At 900 °C, phase formation of the CoSi$_2$ with (100) crystallographic orientation was completed. Decomposition of the CoSi$_2$(400) phase was again observed, but this time at a lower temperature, i.e. 900°C. This means that the use of the Ta cap layer results in single-texture CoSi$_2$ layer with (100) orientation at 800°C.

However, XRD spectra of the heat-treated Ag/W/Co/Si(100) multilayer (not shown here) indicated a different behavior comparing to the Ta capped system [10]. At 500°C, the Ag(111) peak is mainly observed without any phase formation. This observation is well consistent with the results obtained by the Rs measurement. At 700°C, W silicide was formed and the first CoSi$_2$ peak with (331) orientation was observed. At 800 °C a considerable amount of CoSi$_2$ phase formed in (331), (111) and (200) orientations. This shows that the W cap layer could not cause to grow a single-texture CoSi$_2$ layer at the Co/Si interface, instead of the W interlayer. At this temperature, also, no W silicide was observed, and instead, some low intense peak relating to W with (110) and (200) orientations appeared. In addition, the preferred orientation of the crystallized Ag was identified (200), at this temperature. These features can be considered as the main reasons for decreasing the Rs value in 750-800°C. In fact, formation of CoSi$_2$ at the Co/Si interface substantially prevents Si and W interdiffusion, at this temperature range. At a higher temperature (900°C), the CoSi$_2$ phase was not formed due to its decomposition, and so, Si and W interdiffusion leads to reappearance of the W silicide phase.

4. Conclusions
Solid state reaction of Co layer with Si(100) substrate in Ta or W capped and intermediated systems has been studied. Single crystalline CoSi$_2$ layer was grown in the systems having Ta cap and inter layers. But, the epitaxial CoSi$_2$ layer formed in these systems showed a thermal instability at high temperatures (about 900 and 1000 °C, respectively) due to decomposition of the CoSi$_2$ layer and formation of Co$_2$Ta phase. For the systems containing W cap or inter layers, it has been found that the W cap layer is not effective in epitaxial phase formation of CoSi$_2$ layer. Instead, the W interlayer causes formation of single crystalline CoSi$_2$ layer with suitable thermal stability at 900-1000°C.

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Figure 3. XRD spectra of the Co/Ta/Si(100) system annealed at a) 550, b) 700, c) 800, d) 900, and e) 1000 °C.

Figure 4. XRD spectra of the Ag/Ta/Co/Si(100) system annealed at a) 500, b) 700, c) 750, d) 800 and e) 900 °C.

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