Boron Redistribution during Silicidation Process of Titanium-Silicon System

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Redistribution behavior of B during silicidation process of titanium-silicon system at 923 K has been examined by SIMS. Amorphous TiSix layer forms between unreacted Ti and $TiSi_2$. B accumulates in TiSix layer during silicidation process. The concentration of B in TiSix layer increases with silicidation by a snowplow effect.

1. Introduction

Titanium disilicide ($TiSi_2$) is used in very large scale integrated circuits (VLSI) as a self aligned silicide (SALICIDE) and barrier layer, because of its high electrical conductivity and high reactivity with Si about 900 K. One of the most important application of Ti silicide is contact material with Si substrate at the bottom of contact hole. Contact resistance deeply depends on the concentration of dopants at silicide / Si interface.[1] During annealing process for silicidation, dopants diffuse into silicide from Si substrate. This may change doping profiles and concentration of dopants at the interface that affects the contact resistance. Therefore, redistribution of dopants in silicide is an important issue.

Redistribution of impurities in silicides has been investigated.[2-8] However, dopants diffusion from Si substrate during silicidation process is still open to the question. In the present study, the silicidation at 923 K has been examined to make clear the origin and the mechanism of redistribution behavior of B during silicidation process of titanium-silicon system.

2. Experiment

2-1. Materials

The p-type Si wafers of 1.5×10^{-2} Ωcm resistivity and <100> orientation were used in the present study. The wafers were cleaned by 6 mass% BHF (NH_3+NH_4F), rinsed with pure water and dried with air gun before loading into a DC magnetron sputtering system. Ti and subsequently TiN were deposited on the wafers in Ar and N_2 atmosphere respectively to form a TiN(100 nm) / Ti(270 nm) / Si structure. Annealing processes for silicidation were conducted at 927 K in N_2 purged vacuum system with sponge-Ti to reduce partial pressure of O_2 in the system.

2-2. Analysis

X-ray diffraction (XRD) was applied for phase identification of as-deposited and annealed samples. Cross sectional transmission electron microscopy (TEM) was used to elucidate the grain microstructure of silicide, interface roughness and distribution of the compound particles. The phases were determined by selected area diffraction (SAD) and energy dispersive spectroscopy (EDS) analysis. The TEM samples were prepared by focused ion beam (FIB) after deposition of 500 nm TiN layer to protect the surface of samples during FIB process. The variations of B profiles were studied by secondary ion mass spectrometry (SIMS). A 7.0 keV O_2^+ ion beam was used for getting positive secondary ions.

3. Results

Figure 1. shows XRD patterns of as-deposited sample and annealed samples at 923 K. The XRD pattern of as-deposited sample exhibits strong diffraction peaks of hexagonal Ti 100 and Ti 002 with a sharp peak of Si 200. No peak of TiN is observed. This indicates that Ti

layer crystallizes with strong orientation and a large part of TiN layer is in amorphous state as deposition. After 0.6 ks annealing, sharp diffraction peaks of C49-$TiSi_2$, which is a thermodynamically metastable phase, are detected. Strong diffraction peaks of C54-$TiSi_2$, which is a stable phase, is observed after 18 ks annealing.

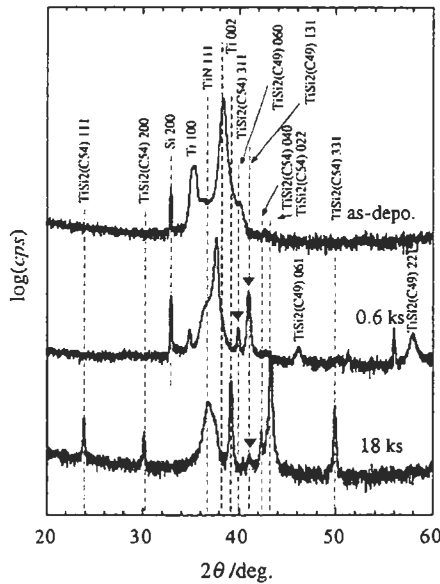

Figure 1. XRD profiles of as-deposited and annealed samples at 923 K.

Figure 2. shows bright field image of annealed sample at 923 K for 0.6 ks. The picture presents the protective TiN / TiN / Ti / TiSix / $TiSi_2$ / Si structure confirmed by SAD and EDS.

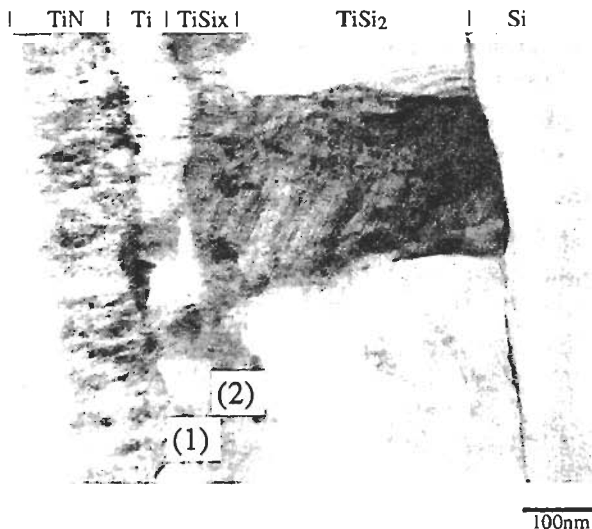

Figure 2. TEM image of annealed sample at 923 K for 0.6 ks.

The SAD pattern obtained from the (1) layer exhibits the spots of hexagonal Ti 100. The EDS analysis also proves that this layer is unreacted Ti. The SAD pattern obtained from the (2) layer contains discrete diffraction spots arranged in discontinuous circles. This indicates that the (2) layer is composed of nanocrystallin Ti silicides in amorphous like state. EDS analysis detects that composition of this layer is TiSix ($0<x<2$).

Figure 3. shows SIMS depth profiles of B and Si. The $TiSi_2$ / Si interface is shifted to higher sputter-etching time with silicidation. In the first 0.6 ks annealing, B diffuses into $TiSi_2$ layer and accumulates in TiSix layer. B profile makes small peak, which is shifted to TiN with silicidation. B accumulates heavily in TiSix layer existing between TiN and $TiSi_2$ after 18 ks annealing. The B^+ ion counts at the top of the peak is higher by about two orders of magnitude than that of in $TiSi_2$. No B accumulation at the $TiSi_2$ / Si interface has been observed.

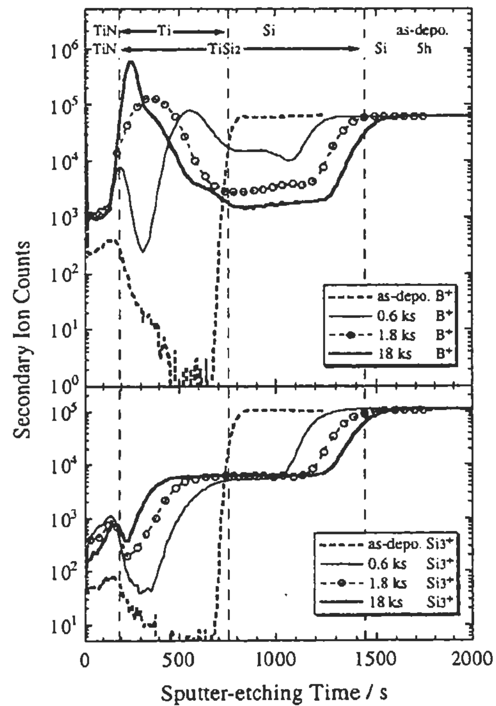

Figure 3. SIMS depth profiles of B and Si in as-deposited and annealed samples at 923 K.

4. Discussions

Maex et al.[7,8] concluded that B accumulated in unreacted Ti layer during Ti silicidation process. They implied that Ti-B

compound formation leaded to accumulation of B in unreacted Ti layer. In the present study, however, SIMS results clearly proves that B accumulates in TiSix layer which exists between unreacted Ti and crystalline $TiSi_2$. No XRD result and TEM observation ascertain the formation of Ti-B compound during silicidation. TiSix layer where B is condensed is shifted toward TiN layer with silicidation and the formation of Ti-B compound should suppress subsequent redistribution of B. The solubility of B in TiSix and $TiSi_2$ has not been reported. However, it is reasonably considered that the solubility of B in TiSix layer should be high, whereas that in crystalline $TiSi_2$ and Ti should be low. Activity of B in TiSix layer should be lower for formation of Ti-B compound(TiB_2) under the condition of present study. The effect of $TiSi_2$ phase transformation is negligibly small for B redistribution because of the small solubility of B in $TiSi_2$.

Gas et al.[2,3] reported that implanted B appeared to be quite immobile in $TiSi_2$ during annealing at 1073 K for 1.8 ks, because of a very low solubility in $TiSi_2$. In the present study, Ti layer of about 100 nm thickness reacts with Si during 0.6 ks annealing. The value of $(Dt)^{0.5}$ of B in single crystalline Si is about 5.2 nm at 923 K for 0.6 ks.[9] It should be disregarded that B diffuses inward the Si substrate during silicidation process. No B accumulation has observed at the $TiSi_2$ / Si interface after silicidation process. It means that the flux of B in $TiSi_2$ is relatively higher than the consumption rate of Si during silicidation. Grain boundary diffusion should play an important role in redistribution of B during silicidation.

Total amount of B in consumed Si increases with silicidation. The concentration of B in TiSix increases with silicidation by a snowplow effect. B concentration in $TiSi_2$ layer decreases because of the crystallization of $TiSi_2$ which has low solubility of B. The grain size of $TiSi_2$ increases with increasing annealing time. This generates the decrease of the grain boundary area where most of B in $TiSi_2$ layer exists. B concentration, therefore, decreases in $TiSi_2$ layer with silicidation. Figure 4. shows the redistribution model of B during Ti silicidation. The lines in the figure represent the concentration profiles of B. In the first stage of the silicidation, amorphous TiSix layer forms between unreacted Ti and Si substrate. Amorphous layer crystallizes to C49-$TiSi_2$ at the Si interface and the structure change to TiN / Ti / TiSix / $TiSi_2$ / Si. B is redistributed by grain boundary diffusion in $TiSi_2$ and accumulates in amorphous TiSix layer. B concentration in $TiSi_2$ layer decreases with silicidation. The TiSix layer is shifted toward TiN layer with silicidation and finally B accumulates in narrow region neighboring TiN layer.

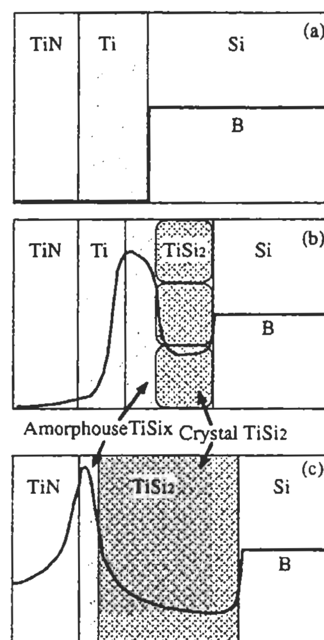

Figure 4. Redistribution model of B during Ti silicidation .

5. Conclusion

The redistribution behavior of B during silicidation process of titanium-silicon system at 923 K has been examined. The metastable phase of $TiSi_2$ (C49 structure) is formed in the first 0.6 ks. C49-$TiSi_2$ is transformed to stable C54-$TiSi_2$ during silicidation process for 18 ks. Amorphous like TiSix layer forms between unreacted Ti and $TiSi_2$. It is reasonably considered that the solubility of B in TiSix layer should be high, whereas that in crystalline $TiSi_2$ and Ti layers should be low. The effect of $TiSi_2$ phase transformation is negligibly small for B redistribution. B accumulates in TiSix layer. The

concentration of B in TiSix increases with silicidation by a snowplow effect. The flux of B in $TiSi_2$ is relatively higher than the consumption rate of Si during silicidation. Grain boundary diffusion of B in $TiSi_2$ should play an important role in redistribution of B during silicidation of titanium-silicon system.

6. References

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