Boron and Oxygen Redistribution during Silicidation Process of Titanium-Silicon System

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(Received November 22, 2001; accepted January 18, 2002)

Redistribution behavior of B and O during silicidation process of titanium-silicon system at 923 K has been examined by secondary ion mass spectrometry and transmission electron microscopy. Amorphous like TiSix forms between unreacted Ti and $TiSi_2$. B accumulates in TiSix and O accumulates in unreacted Ti. The solubility of B and O in Ti and TiSix causes the difference of redistribution behavior of B and O during Ti silicidation.

1. Introduction

Titanium disilicide ($TiSi_2$) is used for a contact material with Si substrate in very large scale integrated circuits (VLSI). Contact resistivity deeply depends on the concentration of dopants at the 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. Native oxide layer of Si (SiO_2) at the Ti / Si interface also increases the contact resistance. The affinity of Ti to oxygen is higher than that of Si [2] and the solubility of oxygen in Ti is extremely high (about 30%).[3] Ti deoxidizes SiO_2 and removes the oxide layer during silicidation process. However, scale down of VLSI demands a shrinkage of contact hole and a decrease of the Ti thickness at the bottom. Therefore, deoxidation of SiO_2 and redistribution of O during silicidation has become significant subject.

Redistribution of impurities in silicides and redistribution of O during silicidation process have been investigated.[4-10] However, dopants diffusion from Si substrate and the mechanism of O redistribution during silicidation process are still open to the question. In the present study, Ti-silicidation at 923 K has been examined to make clear the origin and the mechanism of redistribution behavior of B and O during silicidation process of titanium-silicon system.

2. Experiment

2.1 Materials

The p-type Si wafers of $1.5x10^{-2}$ Ωcm resistivity and <001> orientation were used in the present study. The wafers were cleaned by 6 mass% BHF (NH_3+NH_4F), rinsed with pure water 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 the TiN(100 nm) / Ti(270 nm) / Si structure. Annealing processes for silicidation were conducted at 927 K in a N_2 purged vacuum system with Ti flake to reduce partial pressure of O_2 in the system.

2.2 Analysis

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. TEM samples were prepared by focused ion beam

(FIB) after deposition of 500 nm TiN to protect the surface of samples during FIB process. The variations of B and O profiles were studied by secondary ion mass spectrometry (SIMS). A 7.0 keV O_2^+ ion beam was used for detecting positive secondary ions and a 10.0 keV Cs^+ ion beam was for negative secondary ions.

3. Results

Figure 1. shows cross sectional bright field images and SAD patterns of the annealed sample at 923 K for 1.8 ks. The SAD pattern obtained from the point (1) and (2) exhibits the spots of C54-$TiSi_2$ and TiN respectively. The SAD pattern obtained from the point (3) contains discrete diffraction spots arranged in continuous circles. This indicates that the point (3) is composed of nanocrystalline Ti silicides in amorphous like state. The composition of point (3) is assigned to TiSix ($0<x<2$) by EDS analysis. The SAD pattern of the point (4) exhibits the spots of hexagonal Ti. EDS analysis also proves that point (4) is unreacted Ti with small amount of O.

Figure 2. shows SIMS depth profiles of B, O and Si. The horizontal axis presents the distance from the surface, which is converted sputter-etching time by SIMS profiles and TEM observation. The $TiSi_2$ / Si interface is shifted to deeper distance with silicidation. In the first 0.6 ks annealing (b), B diffuses into $TiSi_2$ and accumulates in TiSix. There is a small peak in the B profile, which is shifted to TiN with silicidation. O is uniformly redistributed in Ti in the first 0.6 ks annealing and the O^- ion counts heavily decrease in $TiSi_2$. After 1.8 ks annealing (c), the B^+ ion counts decrease in $TiSi_2$ and the peak of B profile becomes dull near TiN. There is a sharp peak in the O profile at the TiN / $TiSi_2$ interface after 1.8 ks annealing. B accumulates heavily in TiSix existing between TiN and $TiSi_2$ after 18 ks annealing (d). The B^+ ion counts at the top of the peak is higher by about three orders of magnitude than that of in $TiSi_2$. The O profile of 1.8 ks annealing is close to that of 18 ks annealing.

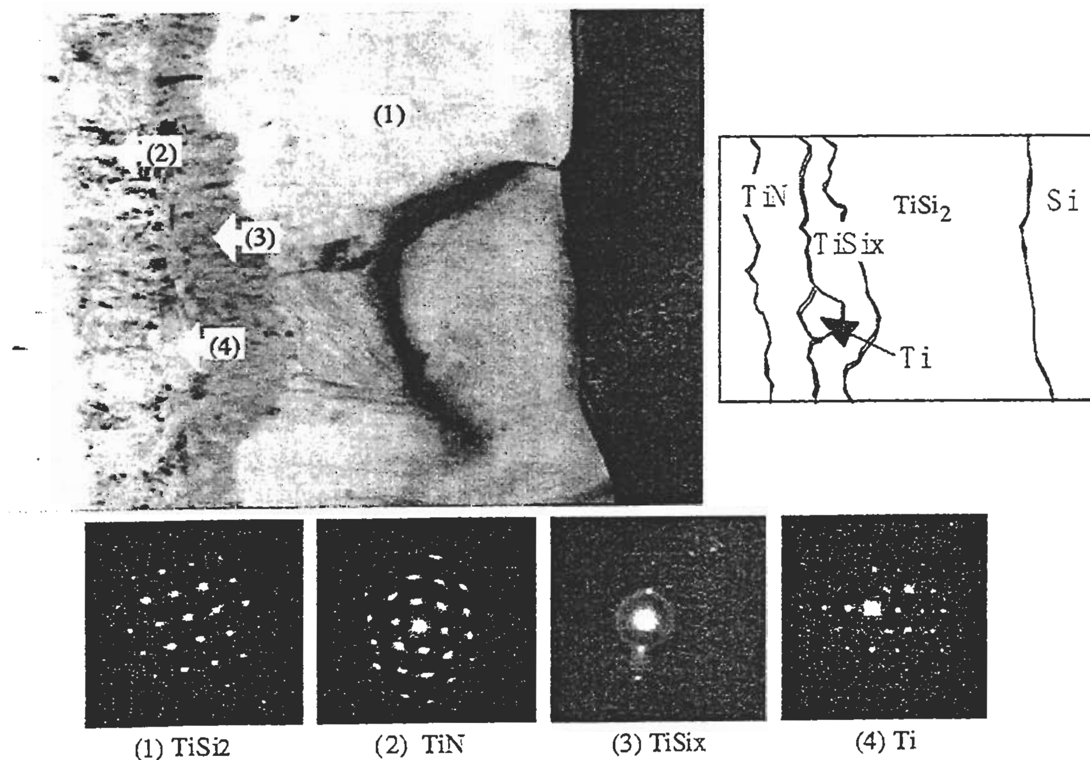

Figure 1. cross sectional bright field images and SAD patterns of the annealed sample at 923 K for 1.8 ks.

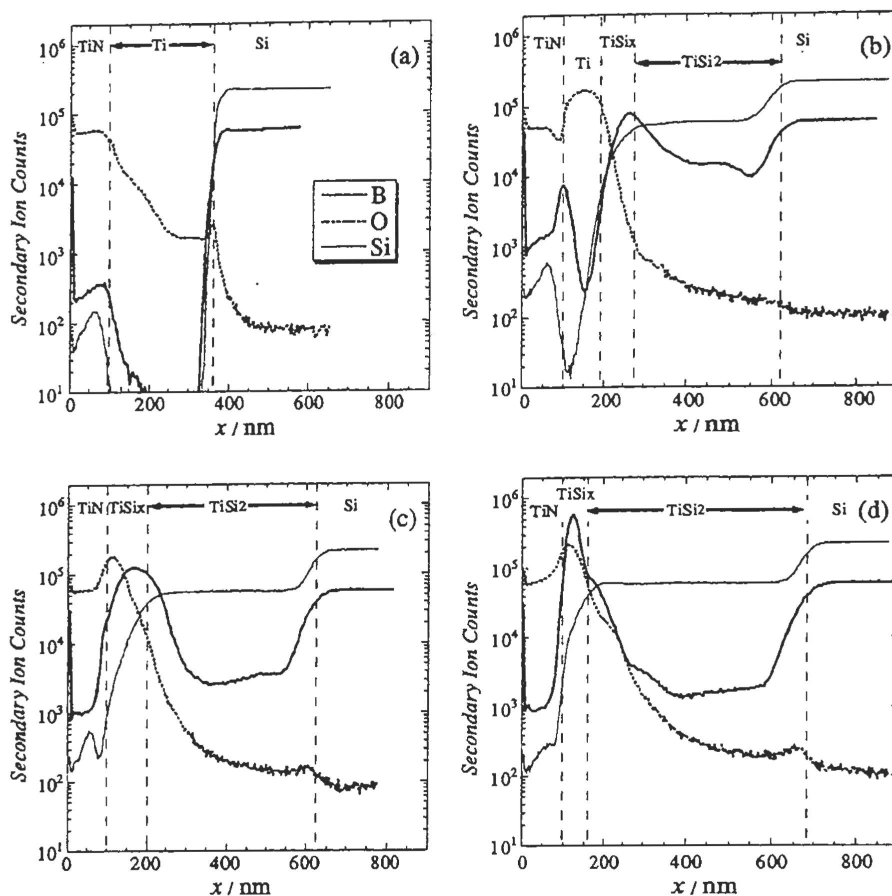

Figure 2. SIMS depth profiles of B, O and Si in (a) as-deposited and annealed samples at 923 K for (b) 0.6 ks, (c) 1.8 ks and (d) 18 ks.

4. Discussions

Gas et al. [4,5] 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 $TiSi_2$. Probst *et al.* [6] reported diffusion of B in $TiSi_2$ and $TaSi_2$. They showed that B was quickly immobilized by boride formation, because of low solubility of B and As in silicide. In the case of the concentration of B was low, however, fast diffusion occurred by high diffusivity along the grain boundaries and lower lattice diffusion within grains. Present authors [7] have investigated the redistribution of B during silicidation process of titanium-silicon system. We concluded that the concentration of B in TiSix increases with silicidation by the snowplow effect and that grain boundary diffusion plays an important role in redistribution of B in $TiSi_2$.

Several works [8-10] have been reported that O is redistributed in Ti uniformly in the early stage of annealing and that O is snowplowed toward the surface with silicidation. TEM observation and SIMS profiles of the present study show that O accumulates in unreacted Ti. The solubility of O in Ti is extremely high [3] and that in TiSix and crystalline $TiSi_2$ is probably low. The thickness of unreacted Ti decreases with silicidation and O is redistributed toward TiN by a snowplow effect. The solubility of B and O in Ti and TiSix causes the difference of redistribution behavior of B and O during Ti silicidation.

Figure 3. shows the redistribution model of B and O during Ti silicidation. The lines in the figure represent the concentration profiles of B and O. In the early stage of the silicidation, amorphous TiSix forms between unreacted Ti

and Si substrate. The amorphous silicide crystallizes to C49-$TiSi_2$ at the Si interface and the structure change to TiN / Ti / TiSix / C49-$TiSi_2$ / Si.[7] $TiSi_2$ transforms from C49 to C54 structure after lengthy silicidation. B is redistributed by grain boundary diffusion in $TiSi_2$ and accumulates in amorphous TiSix. B concentration in TiSix increases and that in $TiSi_2$ decreases with silicidation. The TiSix is shifted toward TiN and finally B accumulates in narrow region neighboring TiN. O is redistributed in Ti uniformly in the early stage of annealing. O accumulates in unreacted Ti by the lattice diffusion in Ti. The thickness of unreacted Ti decreases with silicidation and O is redistributed toward TiN by a snowplow effect.

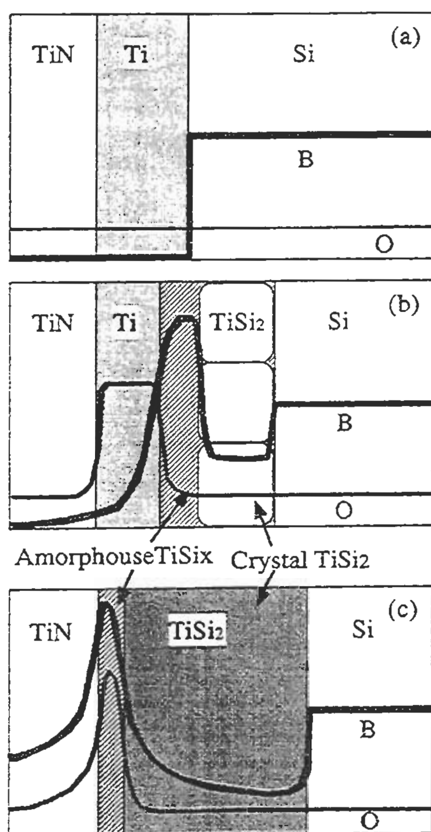

Figure 3. Redistribution model of B and O during Ti silicidation : (a) as-deposited, (b) during silicidation process and (c) after silicidation.

5. Conclusions

Redistribution behavior of B and O during silicidation process of titanium-silicon system at 923 K has been examined. Amorphous like TiSix forms between unreacted Ti and $TiSi_2$. B accumulates in TiSix and O accumulates in unreacted Ti. The concentration of B in TiSix increases with silicidation by a snowplow effect. Grain boundary diffusion plays an important role in redistribution of B in $TiSi_2$. O is redistributed in Ti uniformly in the early stage of annealing. High solubility of O in Ti allows the rapid redistribution by the lattice diffusion. The thickness of unreacted Ti decreases with silicidation and O is redistributed toward TiN by a snowplow effect. The solubility of B and O in Ti and TiSix causes the difference of redistribution behavior of B and O during Ti silicidation.

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