The Properties of Nitrogen Implanted Tungsten Diffusion Barrier for Cu Metallization

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Abstract

N^+ beam modified diffusion barriers have been proposed for Cu metallization. The crystalline phases of W and Ti thin films change from polycrytalline to amorphous phase by the N ion implantation of $1 \sim 3 \times 10^{17}$ atoms/cm^2. The comparison between these amorphized diffusion barriers and the conventional W and TiN films shows that the amorphized W and Ti diffusion barriers are superior to the conventional W and TiN for protecting the Cu diffusion at the annealing temperature range 600°C ~ 800°C for 30 min. This is a worldwidely new and excellent result on the high temperature thermal stability of diffusion barrier.

1. Introduction

Recently, Si VLSI device fabrication process needs multi-level metallization due to several reasons for the planarization of topological surface, improvement of adhesion, reliability and thermal stability of interconnection. Furthermore, multi-level metallization process influences critical effects on electrical performance of VLSI device, reliability, scale down and data process speed. Typically, reliability and electrical performance of VLSI devices are strongly related with the properties of diffusion barrier which is used for preventing the interaction of metal and Si. Therefore, materials for diffusion barrier are now intensively studied by many researchers. Among several metal nitrides and oxides, refractory metal nitrides such as TiN, WN, and TaN are most popularly investigated [1,2] and the crystal phases of these materials are poly or micro-crystalline phases. Nowadays, KIST and Caltech teams insist that amorphous phase is superior to these poly or microcrystalline films since amorphous phase eliminates diffusion paths of Cu through grain boundaries.[3-5]

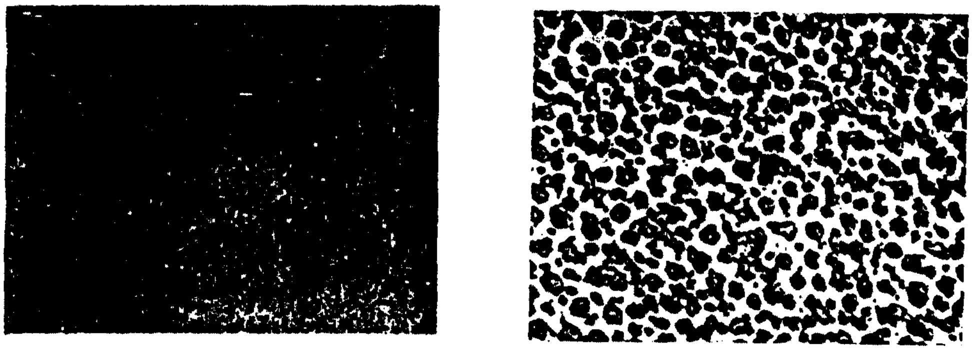
In this work, we have proposed a new method to prepare high temperature thermally stable diffusion barrier. It is to implant an ion among the several ions such as N, B, Si and O ions into the metal thin film, resulting in amorphized thin film. This idea is taking advantages of ion beam modification of metal/semiconductor interface by controlling several parameters such as dosage and energy in ion implantation techniques. We expect that this method can offer some unique advantages such as reducing the fabrication steps, cost down and easy processing. Although there is still several problems such as practical application and how to eliminate Si surface damage, it is also expectable that this work explains clearly the effect of amorphized diffusion barrier.

2. Experiment

We used (100) oriented p-type Si wafers. After RCA cleaning, we deposited 5~600Å polycrystalline W thin film on Si substrate in a home made parallel type cold wall PECVD reactor with the gas flow ratio of WF_6/H_2 fixed at 1/25. The total pressure of CVD reactor was set at 0.5 Torr, the deposition temperature was fixed at 350°C and rf power density is 0.7 W/cm^2. Comparable thickness Ti and TiN films were deposited by RF sputtering method at 200°C. In order to prepare the N ion implanted W (W-N$^+$)and the N ion implanted Ti (Ti-N$^+$) layers at the interface of each metal and Si substrate, N ions with 3×10^{17}ions/cm^2 were implanted on W and Ti layers by the acceleration energies of 60 ~ 80 KeV. MOCVD Cu deposition was carried out on TiN, Ti-N$^+$, W and W-N$^+$. 1500~2000 Å thick Cu films were deposited on these diffusion barriers using (hfac)Cu(vtms) as a metal organic precursor. The Cu deposition temperature was fixed at 200°C. After Cu deposition thermal stabilities of these diffusion barriers were investigated with post annealing process at 600 ~ 800°C for 30min in N_2 ambient. Crystallinity, interfacial reaction and surface defect of each diffusion barrier were determined with X-ray diffraction (XRD), AES, RBS , Nomarski microscope and cross sectional TEM.

3. Results and Discussions

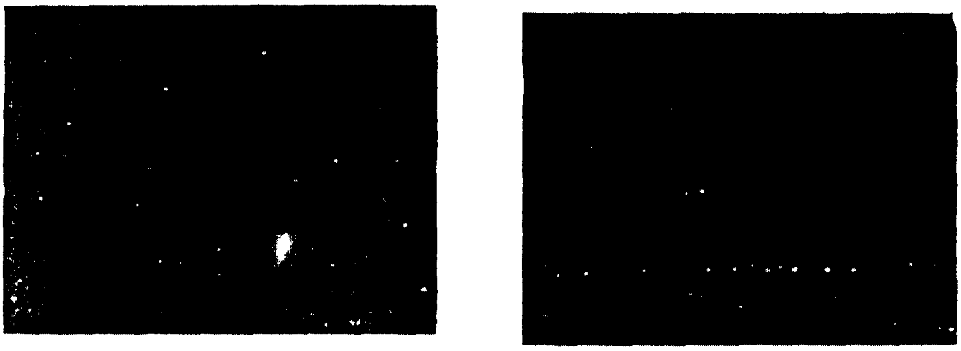
Fig. 1(a) shows Nomarski micrographs for Si/TiN/Cu annealed at 600°C. After removing TiN/Cu, surface morphologies reveal defects generated by Cu diffusion. This figure obviously indicates that the conventional TiN cannot protects Cu diffusion at the annealing temperatures higher than 600°C. As the annealing temperature increases from 600°C to 800°C, the density of etch pits increases and their sizes become larger. However, the N implanted Ti thin film is more effective than TiN for preventing Cu diffusion as shown in Fig. 1(b) where numberous specks are not defects but stains remained on surface. This figure reveals that defect density is very low after annealing at 700°C and even if annealing is done at 800°C for 30min, defect density is incredibly lower than Fig. 1 (a). But sizes of defect become larger. It can be explained that the Ti-N$^+$ plays the excellent diffusion barrier for Cu atoms comparing with the conventional TiN film because of eliminating grain boundaries by N$^+$ implantation on the Ti layer, resulting in the amorphized Ti- N$^+$ layer. However, as shown in Fig. 1(b), Cu atoms might diffuse through the local pathway in the Ti-N$^+$ which seems to be a sink pipe for the Cu diffusion. Consequently, larger size defects with lower density are observed on the Ti-N$^+$. Fig. 2(a) shows Nomarski micrographs for Si/W/Cu annealed at 600°C. It shows the same trend with the TiN diffusion barrier. Many defects are observed after



(a) (b)

Fig. 1 Nomarski micrographs for (a) Si/TiN/Cu annealed at 600°C and (b) Si/Ti-N$^+$/Cu annealed at 700°C

annealing at 600°C, whereas W-N$^+$ perfectly prevents Cu diffusion as shown in Fig. 2(b) revealing that there are no defects even at 800°C annealing for 30min. To our knowledge, this is the highest temperature at which W diffusion barrier prevents Cu diffusion. We try to investigate the AES depth profiles of Si/W-N$^+$/Cu scheme before and after annealing. Fig. 3(a) shows AES depth profile of as implanted W-N$^+$ film. The projection range (Rp) of N$^+$ exists on the interface of W and Si. The N profile doesn't change after annealing at 800°C for 30 min. Cu thin film is prepared on these W-N$^+$ diffusion barrier and annealing is done at 800°C for 30min. Fig. 3(b) shows the AES depth profile for the annealed Si/W-N$^+$/Cu structure. In this figure, although the Cu profile extends into the interface of W-N$^+$ and Si, Cu doesn't penetrate into the bulk Si region. Therefore, it can be concluded that the W-N$^+$ diffusion barrier plays



(a) (b)

Fig. 2 Nomarski micrographs for (a) Si/W/Cu annealed at 600°C and (b) Si/W-N$^-$/Cu annealed at 800°C the excellent role of preventing Cu diffusion at 800°C for 30min. Also, interfacial reaction between metal and semiconductor was analyzed by RBS measurement for Si/W-N$^+$/Cu structure after annealing at 800°C for 30min, where the tailing edge of Cu signal doesn't overlap Si signal meaning that there is no reaction between Cu and Si not shown here. In order to study the interface of Si/W-N$^+$/Cu structure, cross sectional TEM was taken after annealing at 800°C for 30min. Fig. 4 shows that the crystalline phase of W-N$^+$ is amorphous and no defect exists at the interface of W-N$^+$ and Si. We believe that this amorphous layer is very effective for preventing the Cu diffusion. But the Si surface region is severely damaged by the N$^+$ implantation. Therefore, it needs to find out an optimum condition to avoid the surface damage on Si by controlling several implantation parameters such as dosage and acceleration energy.

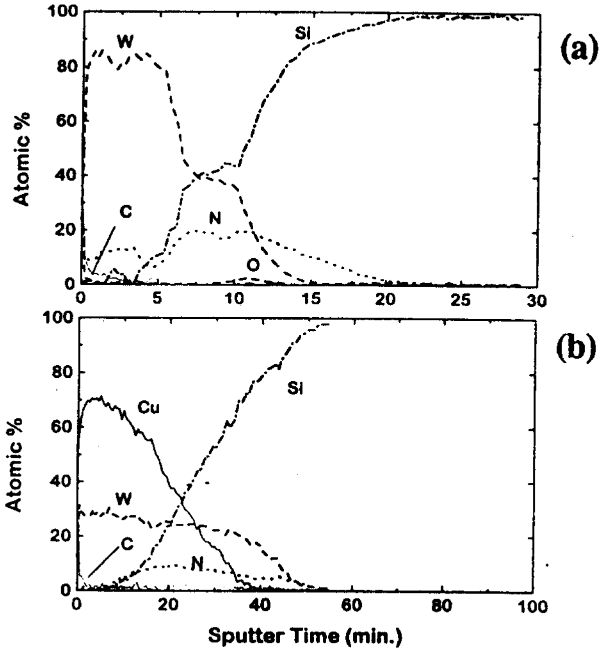


Fig. 3 AES depth profile of
(a) as implanted W-N$^+$on Si
and (b) Si/W-N$^+$/Cu annealed
at 800°C for 30min

Fig. 4 XTEM micrographs
for Si/W-N$^+$/Cu annealed
at 800°C for 30min

XRD pattern for as deposited Cu on Si/W-N$^+$ as shown in Fig. 5(a) shows (111) and (200) oriented Cu peaks. Fig. 5(b) is an XRD pattern of Si/W-N$^+$ /Cu after annealing at 800°C for 30min. These figures show that there are no Cu silicide and W silicide peaks such as Cu_3Si, Cu_4Si, W_5Si_3 and Si_2W. From the experimental results of AES, XTEM and XRD as well as Nomarski micrographs, it is concluded that W-N$^+$. diffusion barrier effectively prevents the Cu diffusion or any reactions of Cu with Si after annealing at 800°C for 30 min.

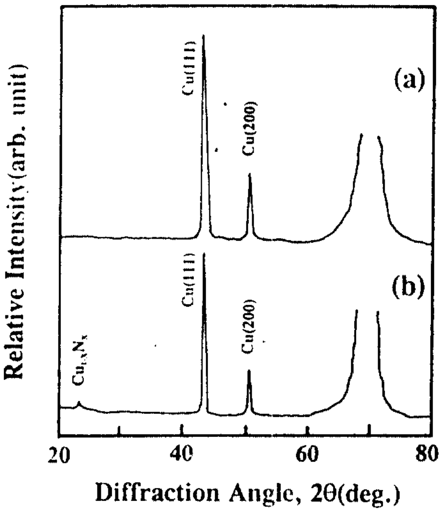


Fig. 5 XRD pattern for (a) as deposited Cu film on Si/W-N^+ and (b) Si/W-N^+/Cu annealed at 800°C for 30min

4. Conclusions

In summary, we have proposed a new method to prepare the high temperature thermally stable diffusion barrier. This method is taking advantages of ion beam modification process of metal/semiconductor interface by controlling several parameters of implantation technique. we demonstrate a new diffusion barrier (W-N^+) is very effective for preventing the Cu diffusion. The excellent properties of W-N^+ is due to the crystalline phase transformation from polycrystalline to amorphous phase by nitrogen ion implantation. Also, we find that Ti-N^+ is also superior to conventional TiN in the properties of diffusion barrier due to the amorphous phase. Therefore. we can conclude that the ion beam modification of metal/semiconductor interface can be an effective method to improve the properties of conventional diffusion barriers and typically the W-N^+ diffusion barrier shows excellent thermal stability even at 800°C for 30 min , which is the highest record of a diffusion barrier for Cu metallization.

Acknowledgement

The author would like to thank professor Liu Xiang Huai, Shanghai Institute of Metallurgy, for implantation experiment.

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