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Enhancement of Barrier Properties in Chemical Vapor Deposited TiN Employing Multi-Stacked Ti/TiN Structure

Ting-Chang CHANG[1,3], Po-Tsun LIU[2], Ya-Liang YANG[3], Jung-Chih HU[4] and Simon M. SZE[2,3]

[1]*Department of Physics, National Sun Yat-Sen University, Taiwan, R.O.C.*
[2]*Department of Electronics Engineering and Institute of Electronics, National Chiao-Tung University, 1001-1 Ta-Hsueh Road, HsinChu 300, Taiwan, R.O.C.*
[3]*National Nano Device Laboratory, 1001-1 Ta-Hsueh Road, HsinChu 300, Taiwan, R.O.C.*
[4]*Department of Materials Science and Engineering, National Tsing-Hua University, Hsinchu, Taiwan, R.O.C.*

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A novel multi-stacked Ti/TiN structure was proposed to enhance the barrier properties of chemical vapor deposited TiN film. Both the chlorine content and the resistivity of the multi-stacked Ti/TiN films are significantly decreased when compared with a single layer of chemical vapor deposited (CVD) TiN film with the same thickness. Secondary ion mass spectrometry (SIMS) data showed that Ti atom distribution is fairly uniform to fill the grain boundary of TiN film. Therefore, the leakage current resulted from junction spiking was further reduced by the grain boundary effects when employing multi-stacked Ti/TiN as diffusion barrier layer instead of a single layer of TiN film.

KEYWORDS: barrier, multi-stacked Ti/TiN, chlorine content, resistivity, boundary effects

1. Introduction

Titanium nitride (TiN) has been widely recognized as an excellent contact barrier between Al and Si, as well as the preferred glue layer for blanket-W deposition.[1–3] TiN film is traditionally deposited by physical deposition methods such as reactive ion sputtering or nitridation of sputter deposited it in nitrogen-containing gases at high temperatures.[4,5] However, sputtering technique is inherently non-conformal, resulting in significant thinning at via and trench edges and walls. It would give poor step coverage and could not meet the demands of ULSI technologies below the subquarter micron level. Therefore, chemical vapor deposited (CVD) TiN has been proposed as an alternative to physical vapor sputtered TiN film, because CVD process usually offers conformal metal growth and ability to coat large area substrates with excellent uniformity at industrially viable growth rates.[6,7)]

The commonly used precursors for CVD TiN processes are titanium tetrachloride ($TiCl_4$) associated with ammonia[8,9] and metallorganic titanium compounds such as tetrakis dimethyl amino titanium (TDMAT)[10] and tetrakis diethyl amino titanium (TDEAT).[11] Both TDMAT and TDEAT have been successfully used to deposit TiN films with good step coverage at temperature below 400°C. However, the as-deposited films are porous and absorb moisture and oxygen when they are exposed to air, resulting in the degradation of film electrical properties. These films also contain organic carbon and hydrogen,[12] and have much higher resistivity than those deposited by sputtering. Another disadvantage of the metallorganic precursors is that they could not be used to deposit metallic titanium films.

In $TiCl_4/NH_3$ based CVD-TiN process, CVD-TiN films could be used as a good diffusion barrier for Al interconnects. However, the incorporation of significant amount of chlorine (Cl) in the film is of major concern for long-term reliability of finished device.[13,14] In addition, the grains of TiN film were of columnar structures.[15,16] When TiN film was used as a barrier layer, Al and Si would interdiffuse through the grain boundary of TiN film after annealing at elevated temperature. The diffusion of Al and Si through the barrier would cause junction spiking, which will exhibit large leakage current or even become electrically shorted.

In this work, a reliable CVD multi-stacked Ti/TiN structure associated with *in situ* NH_3 plasma post-treatment is proposed to enhance the barrier property of TiN. The multi-stacked Ti/TiN is grown by CVD technique. The diffusion barrier properties of the multi-stacked Ti/TiN films were investigated using material analysis techniques and leakage current measurement.

2. Experimental

The Al/TiN/$TiSi_2$/n^+-p and Al/[stacked Ti/TiN]/$TiSi_2$/n^+-p junction diodes were fabricated for the investigation of a single CVD-TiN and a multi-stacked Ti/TiN barrier capability. The starting materials were 6-in., (100)-oriented p-type silicon wafers. After RCA standard cleaning, the wafers were thermally oxidized at 1050°C to grow a 550 nm oxide layer. The contact holes were patterned by photolithographic and reactive ion etching (RIE) techniques. The n^+-p junctions were formed by As^+ implantation on p-type substrate at 40 keV to a dose of $5 \times 10^{15}/cm^2$ followed by furnace annealing at 900°C for 30 min in N_2 ambient.

After the junctions were formed, the wafers were prepared for Ti and TiN or multi-stacked Ti/TiN barrier layer deposition. In this study, both CVD-Ti and CVD-TiN films were deposited using a cluster tool which has two vacuum cassette elevator, a soft sputter etch module, a CVD Ti and a CVD TiN module, and a cool down station. The titanium films were deposited by plasma-enhanced chemical vapor deposition (PECVD) at temperature 590°C using a mixture of $TiCl_4$, H_2, and Ar. The process chamber pressure was 5 Torr and the rf power was 350 W. Metallic Ti and $TiSi_2$ films were formed in contact holes, respectively. Sequentially, samples were transferred to another chamber without exposure to atmosphere depositing TiN films by low pressure chemical vapor deposition (LPCVD) using $TiCl_4$ and NH_3 associated with a N_2 dilution gas. The base vacuum level of the CVD chamber was maintained to be better than 10^{-6} Torr. Total pressure was fixed at 20 Torr when LPCVD TiN film was deposited. The substrate temperature during TiN film growth was maintained at 630°C. The *in situ* NH_3 plasma post-treatment with 500 W was applied to as-deposited TiN films for 300 s. The TiN/$TiSi_2$/n^+-p

junction diodes were thereby formed, which were also labeled as Sample STD. On the other hand, the multi-stacked Ti/TiN films were formed by depositing PECVD Ti and LPCVD TiN film in turn on the $TiN/TiSi_2/n^+$-p substrate with a deposited period of 20 s and 60 s, respectively. Consequentially, $TiN/Ti/TiN/TiSi_2/n^+$-p, $TiN/Ti/TiN/Ti/TiN/TiSi_2/n^+$-p, and $TiN/Ti/TiN/Ti/TiN/Ti/TiN/TiSi_2/n^+$-p samples associated with NH_3 plasma post-treatment for 300 s were manufactured and labeled as Sample (I), Sample (II) and Sample (III), respectively. The total thickness of these multi-stacked Ti/TiN films was 35 nm and the same as the Sample STD, which were confirmed by X-ray transmission electron microscopy (XTEM). After the barrier layer deposition, aluminum alloy (Al–0.5 at.% Cu) was sputter deposited on the TiN and multi-stacked Ti/TiN barrier metal, respectively.

To investigate thermal stability of $Al/TiN/TiSi_2/n^+$-p and Al/[stacked Ti/TiN]/$TiSi_2/n^+$-p junction diodes, the diodes were subjected to thermal annealing at various temperatures ranging from 400 to 600°C for 30 min in N_2 ambient. Leakage currents of n^+-p diodes were measured by a staircase voltage ramp using an HP4145B semiconductor parameter analyzer at reverse bias voltage of 5 V for the barrier study of this contact system. At least 30 diodes were measured in each case. For material analysis, unpatterned samples of barrier/Si structures were also prepared. Sheet resistance of the multilayer structures was measured using a four-point probe, with 51 points measured. Titanium, nitrogen and chlorine concentrations in barrier films were measured by Auger electron spectroscopy (AES) measurements. X-ray diffraction (XRD) analysis using a 30 keV copper Kα radiation was employed for phase identification.

3. Results and Discussion

In situ NH_3 plasma post-treatment is effective in reducing the resistivity of TiN films. Specific details were given in our earlier paper.[14] For the investigation of multi-stacked Ti/TiN films, the resistivity of all samples with a thickness of 35 nm was first measured. Figure 1 shows the resistivity of these samples as a function of the layer number of stacked Ti/TiN films. The resistivity of these samples with the same thickness was decreased with the increase in the layer number of stacked Ti/TiN films. This shows that increasing layer number of stacked Ti/TiN films associated with NH_3 plasma post-treatment effectively contribute to reduce the resistivity of TiN films.

Furthermore, chlorine content in these samples was detected by the analysis of AES depth profile. Figures 2(a) and 2(b) show AES depth profile of Sample STD and Sample (III), respectively. The chlorine concentration in the Sample STD was found to be about 2.8 at.%. As a result, the Sample STD had a higher value of resistivity (~150 $\mu\Omega$-cm). In contrast, the chlorine concentration in the Sample (III) was detected to be about 1.6 at.%, which was lower than that of the Sample STD. A previous study showed that chlorine content in excess of 5 at.% would degrade metal reliability and increase resistivity of TiN film.[9] The chlorine content in the multi-stacked Ti/TiN film was closed to 1.6 at.%. This will make the corrosion in subsequent Al film is eliminated. In addition, it was observed that the concentration of Ti + N was fairly uniformly in the Sample (III) according to AES measurement.

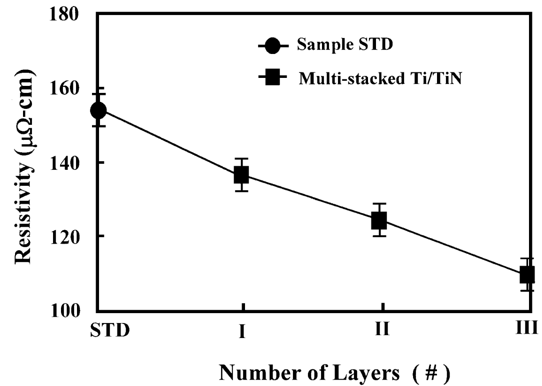

Fig. 1. The resistivity of various samples with *in situ* NH_3 plasma post-treatment for 300 s. Samples are labeled as followed: CVD-$TiN/TiSi_2/n^+$-p (Sample STD), CVD-$TiN/Ti/TiN/TiSi_2/n^+$-p (Sample I), CVD-$TiN/Ti/TiN/Ti/TiN/TiSi_2/n^+$-p (Sample II), and CVD-$TiN/Ti/TiN/Ti/TiN/Ti/TiN/TiSi_2/n^+$-p (Sample III). The thickness of all samples is 35 nm.

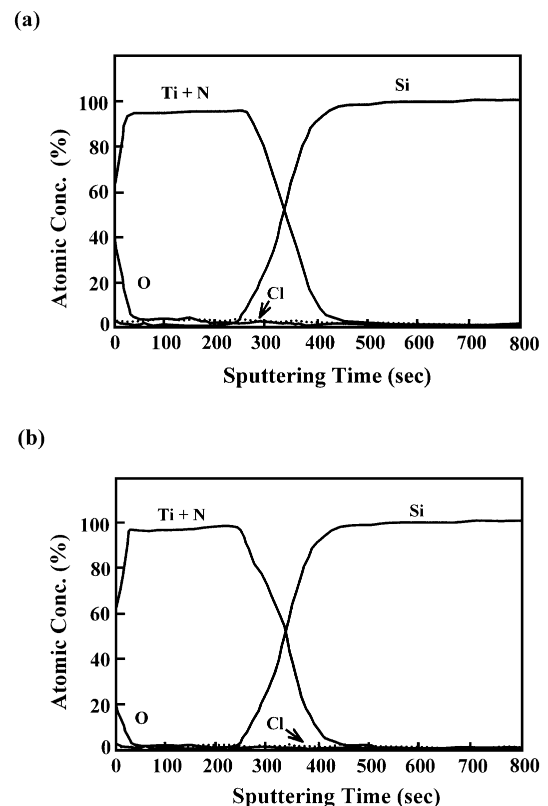

Fig. 2. AES depth profile of different CVD-TiN samples. (a) $TiN/TiSi_2/n^+$-p with NH_3 plasma treatment for 300 s. (Sample STD) (b) $TiN/Ti/TiN/Ti/TiN/Ti/TiN/TiSi_2/n^+$-p with NH_3 plasma treatment for 300 s. (Sample III)

To investigate Ti atom distribution behavior in multi-stacked Ti/TiN films, the $^{47}Ti+N$ and ^{51}Ti depth profiles were measured by secondary ion mass spectrometry (SIMS) for an as-deposited multi-stacked Sample (III), as shown in Fig. 3. It was found that the distribution of Ti atoms is fairly uniformly in multi-stacked Ti/TiN sample. The result is also in agreement with the observation of XTEM image. Figures 4(a) and 4(b) show the cross-section XTEM image of Sample STD and Sample (III), respectively. The interfaces between TiN and $TiSi_2$ in both Samples STD and (III) are rather smooth. In addition, it is clearly observed that the CVD-TiN grains in

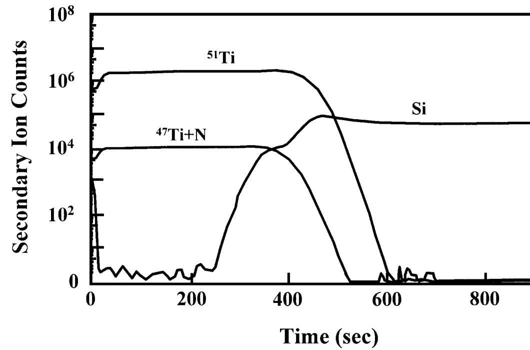

Fig. 3. SIMS depth profiles of TiN/Ti/TiN/Ti/TiN/Ti/TiN/$TiSi_2$/n^+-p sample after being treated with NH_3 plasma for 300 s. (Sample III)

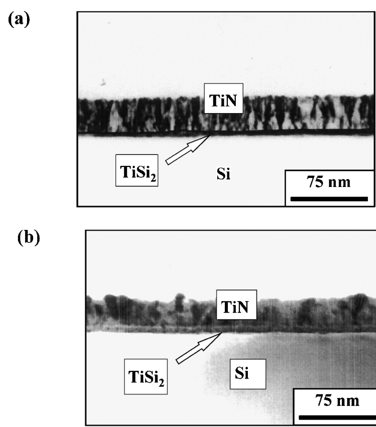

Fig. 4. Cross-section XTEM micrographs for different samples with the same thickness (35 nm). (a) CVD-TiN/$TiSi_2$/Si (Sample STD) (b) CVD-TiN/Ti/TiN/Ti/TiN/Ti/TiN/$TiSi_2$/Si (Sample III)

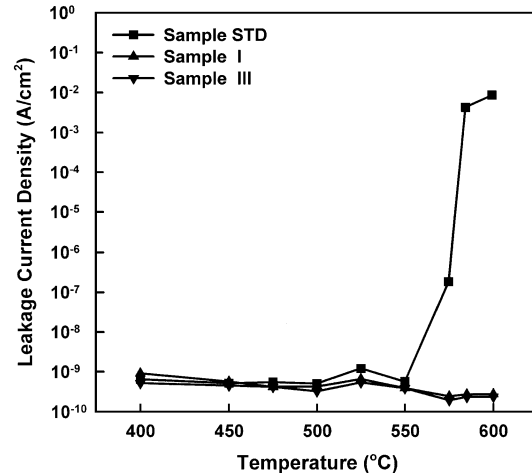

Fig. 5. Leakage current density of n^+-p junction diodes with various types of barrier layer.

Sample STD are columnar structures as shown in Fig. 4(a). However, the TiN grain boundaries and interfaces between Ti and TiN film in multi-stacked Ti/TiN structure seem to be not apparent in the XTEM image. This means that sequent deposition of Ti may stuff into the CVD-TiN grain boundaries, which is also consistence with SIMS data that Ti atoms are distributed fairly uniformly by fast diffusion in TiN films of multi-stacked structure. In addition, a previous study has shown that PECVD Ti deposition rate varied with different substrate.[17] Except for amorphous and crystal Si, the deposition rate of PECVD Ti is rather low on other substrates. As a result, the thickness of PECVD Ti deposited on TiN film for 20 s to form multi-stacked Ti/TiN films is relatively thin. On the basis of above statements, it is reasonably believed that the very thin layer of PECVD Ti layer can effectively fill the grain boundary of TiN film to reduce film resistivity.

Barrier capability of multi-stacked Ti/TiN structure was investigated by evaluating the thermal stability of Al–0.5 at.%Cu/TiN/$TiSi_2$/n^+-p junction diodes using electrical measurements. Figure 5 illustrates leakage current density measured at a reverse bias voltage of 5 V for different multi-stacked Ti/TiN structure annealed at 400–600°C for 30 min. After annealing at 575°C for 30 min, contact systems using Sample STD as barrier layer exhibited large leakage current. This indicates that thermal stability of the Al–Cu/Sample STD/n^+-p junction diodes is severely degraded by the inter-diffusion between Al atoms and Si through the columnar-grains TiN films leading to junction spiking, which will exhibit large leakage current or even electrical shorting. The barrier properties of CVD-TiN film can be significantly improved by multi-stacked Ti/TiN structure with the same thickness. Experimental results show that the thermal stability of multi-stacked Ti/TiN films is superior to a single layer of CVD-TiN film. These results are believed that the very thin PECVD Ti layer deposited on TiN film in multi-stacked Ti/TiN structure may fill the grain boundaries of columnar TiN film to reduce paths for Al/Si interdiffusion. This would make it difficult for junction spiking. As a result, the leakage current of n^+-p junction with multi-stacked Ti/TiN as barrier is lower than that of a single layer of CVD-TiN film. This explanation is also in agreement with the observation of uniform-distributed Ti in SIMS depth profile, as shown in Fig. 3. Therefore, CVD multi-stacked Ti/TiN structure is really effective in enhancing the barrier properties.

4. Conclusion

In this work, increasing layer number of multi-stacked of Ti/TiN films and NH_3 plasma post-treatment technique effectively contribute to reduce both resistivity of TiN films and the chlorine content in multi-stacked Ti/TiN. In addition, SIMS depth profiles of the multi-stacked Ti/TiN sample showed that Ti atom distribution was fairly uniform to fill the grain boundary of TiN film. Electrical measurements indicated the barrier property of multi-stacked Ti/TiN film was superior to that of a single layer of CVD-TiN film. For the n^+-p junction diodes with multi-stacked Ti/TiN barrier, the devices remained stable after annealing at temperatures up to 600°C while severe degradation had occurred in that of a single layer of CVD-TiN barrier with the same thickness.

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