

## An Efficient Improvement for Barrier Effect of W-Filled Contact

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A post CVD-W treatment by  $N_2$  plasma was proposed to suppress the  $WAl_{12}$  formation during the subsequent thermal annealing, and thus improves the thermal stability of W-filled contact. Selective CVD-W was employed to fill the contact hole. Following the W deposition, in situ  $N_2$  plasma treatment was performed prior to Al alloy metallization. Various evidences have shown that this post CVD-W treatment efficiently suppressed the formation of  $WAl_{12}$  and resulted in an improvement on barrier capability of W-filled contact.

### 1. INTRODUCTION

Selective chemical vapor deposition of tungsten (CVD-W) is one of the most attractive techniques for filling contact hole for the ULSI applications. Tungsten was considered to be a good contact barrier to protect shallow junctions from aluminum spiking<sup>1-2</sup> and attain low contact resistance<sup>3-4</sup>. However, the formation of W-Al alloy ( $WAl_{12}$ )<sup>5-6</sup> at 450 °C degrades the barrier property of W contacted diodes. Nitridation of tungsten is expected to improve the tungsten's barrier property, because metal nitrides are generally more chemically stable than the corresponding metals, and they have higher possibilities of suppressing reactions between Al and Si. A number of studies have reported on the improvement of the barrier property of W using furnace  $NH_3$  nitridation<sup>7</sup>, rapid thermal  $NH_3$  nitridation<sup>8</sup>, and  $N_2$  plasma ECR nitridation<sup>9</sup>. In this work, we developed a simple post CVD-W treatment for improving the barrier capability of W with respect to Al. According to this scheme, a thin W nitride layer was formed on the surface of a selective CVD-W layer by in situ post  $N_2$  plasma treatment.

### 2. EXPERIMENTAL

The starting material was n-type (100)-oriented Si wafers with 10-20  $\Omega$ -cm nominal resistivity. After the formation of  $p^+n$  junction, a 4000Å thickness of TEOS layer was deposited on all the wafers, and contact holes with sizes ranging from 1.5 to 3  $\mu m$  were then defined on the wafers. In this work, the CVD-W was conducted with conditions illustrated as follows: substrate temperature 300 °C, total gas pressure 100 mtorr,  $WF_6$  flow rate 20 sccm,  $SiH_4$  flow rate 10 sccm, and  $H_2$  carrier gas flow rate 1000 sccm. After the selective CVD-W, these wafer were divided two groups. One group of wafers were treated with in situ  $N_2$  plasma without expose to the air with conditions illustrated as follows: total gas pressure 25 mtorr, plasma power 50 W and  $N_2$  flow rate 80 sccm. Finally, Al alloy metalization was applied followed by 30 min sintering at 400°C. Junction leakage was measured using the junction monitor which has a junction area of  $100 \times 100 \mu m^2$  and a total of 25 contact holes, as shown in Fig. 1. Contact resistance was measured using the four-terminal Kelvin structure. X-ray diffraction (XRD) analysis was used for

phase identification. X-ray photoelectron spectroscopy (XPS) was used to analyze the Al/W interface.

### 3. RESULTS AND DISCUSSIONS

Figure 2 shows the sheet resistance of W film versus plasma treatment time. The sheet resistance increases with the plasma treatment time in the first two minutes, and then reaches a saturation value, presumably because a thin layer of W-nitride has formed over the W surface and the nitridation process ceases. Figure 3 shows the measured sheet resistance of the Al/W/Si structure annealed at various temperatures. The  $N_2$  plasma treated samples show no change in sheet resistance up to 575 °C annealing, while the control samples show drastic increase in sheet resistance following 550 °C anneal. The resistance increase of the Al/W/Si structure may reflect the consumption of conductive aluminum due to the formation of  $WAl_{12}$ , as confirmed by the x-ray diffraction pattern shown in Fig. 4. With a post  $N_2$  plasma treatment prior to the Al metallization, it was possible to suppress the compound formation (Fig. 4b), while the  $WAl_{12}$  compound appeared apparently on the Al/W/Si sample after 550 °C annealing (Fig. 4a). Statistic distributions of reverse biased leakage currents for the Al/W/ $p^+n$  junction diodes annealed at temperatures higher than 550 °C are illustrated in Fig 5. Below 550 °C annealing, both samples remained stable; after anneal at 550 °C, small reaction of both samples became slightly degraded (Figs 5a2 and 5b2). The junction characteristics of the Al/W/ $p^+n$  diode with  $N_2$  plasma treatment still remained slightly degraded following 575°C anneal (Fig. 5b3), while those without  $N_2$  plasma treatment were drastically degraded (Fig. 5a3). It is clear that the thermal stability of electrical characteristic can be improved by  $N_2$  plasma treatment. Figure 6 shows the contact resistance versus contact area for the W contacted junction diodes using the Kelvin structure. Contact resistances of the Al/W/ $p^+n$  diodes with  $N_2$  plasma treatment are slightly higher than those of the diodes without  $N_2$  plasma treatment. With annealing at elevated temperatures, the contact resistance remained unchanged up to 575 °C for the plasma treated Al/W/ $p^+n$  samples, while drastic increase of contact resistance occurred for the samples without  $N_2$  plasma treatment, as shown in Fig. 7. For the samples observed, the degradation of contact resistance is similar to

the degradation of sheet resistance; they are all due to the formation of  $WAl_{12}$  compound. The  $N_2$  plasma treatment efficiently suppressed the formation of  $WAl_{12}$  and improved the thermal stability of the W contacted junction diodes up to 575°C. In order to study the Al/W interface change due to the thermal treatment, XPS analysis was made on the plasma treated Al/W/Si samples by recording the  $N_{1s}$  and  $W_{4f}$  signals, as shown in Fig. 8. The total  $Ar^+$  ion sputtering time was 10 min; the ion sputtering was performed until the ion reached the Al/W interface. It can be seen that,  $N_{1s}$  peak (binding energy (B.E.) = 397.730 eV) appears at the Al/W interface. It is clear that nitrogen bonds exist at the W surface. The XPS analysis also showed the  $W_{4f_{7/2}}$  (B.E. = 31.241 eV) and the  $W_{4f_{5/2}}$  (B.E. = 33.477 eV) peaks. Both signals increased with the sputtering time until the ion reached the Al/W interface.

#### 4. CONCLUSIONS

In this work, thermal stability of the W contacted  $p^+n$  junction diodes with an in situ  $N_2$  plasma treatment on the selective CVD-W surface was investigated. The  $N_2$  plasma treatment retarded the  $WAl_{12}$  formation, and thus improved the thermal stability of the Al/W/Si structure up to 575 °C. This scheme of treatment also improved the thermal stability of the Al/W/ $p^+n$  junction diodes up to 550 °C. The post CVD-W treatment with in situ  $N_2$  plasma is a simple,

practical and efficient method of improving the barrier capability of W-filled contact.

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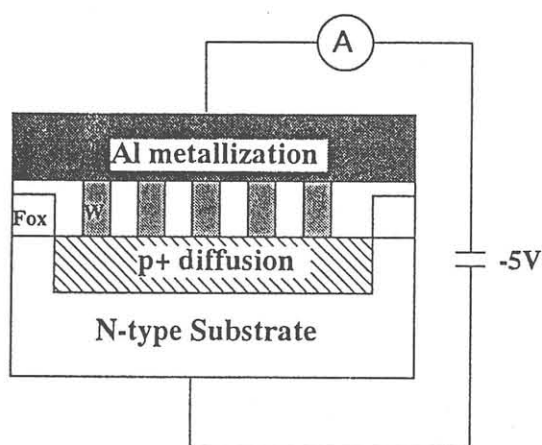


Figure 1 Junction leakage monitor.

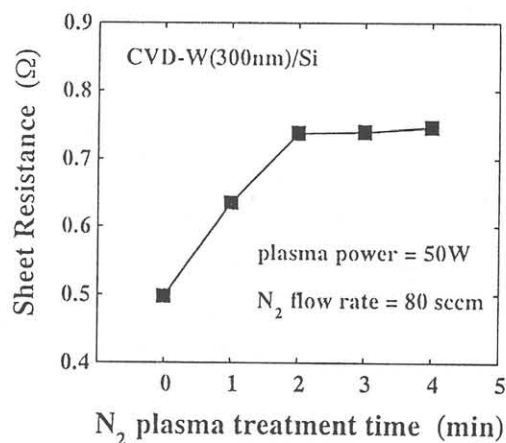


Figure 2 Sheet resistance of W film vs.  $N_2$  plasma treatment time.

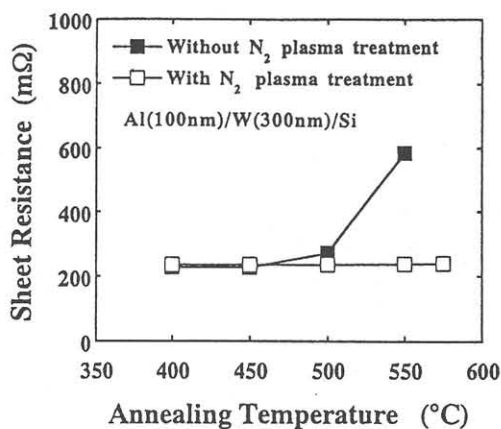


Figure 3 Sheet resistance vs. annealing temperature for the Al/W/Si samples with and without N<sub>2</sub> plasma treatment.

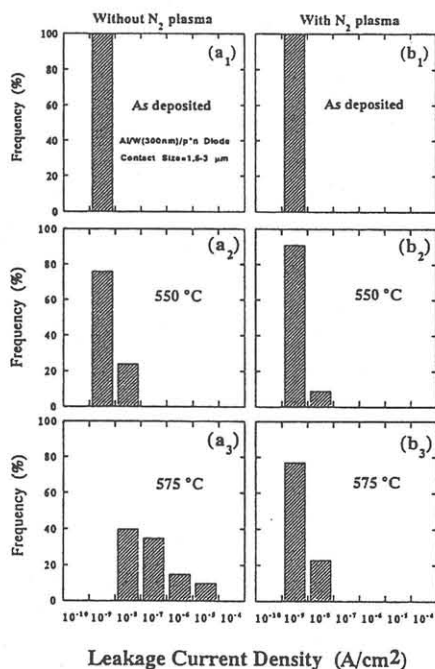


Figure 5 Histograms showing the distribution of reverse biased leakage current density measured at -5 volts for the Al/W/p<sup>+</sup>n junction diodes (a) without and (b) with N<sub>2</sub> plasma treatment.

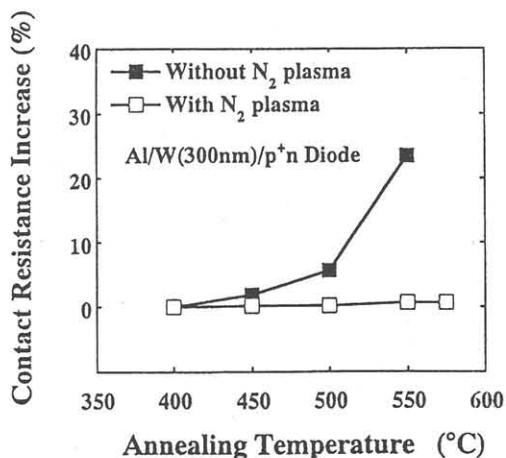


Figure 7 Contact resistance increase vs. annealing temperature for the Al/W/p<sup>+</sup>n diodes with and without N<sub>2</sub> plasma treatment.

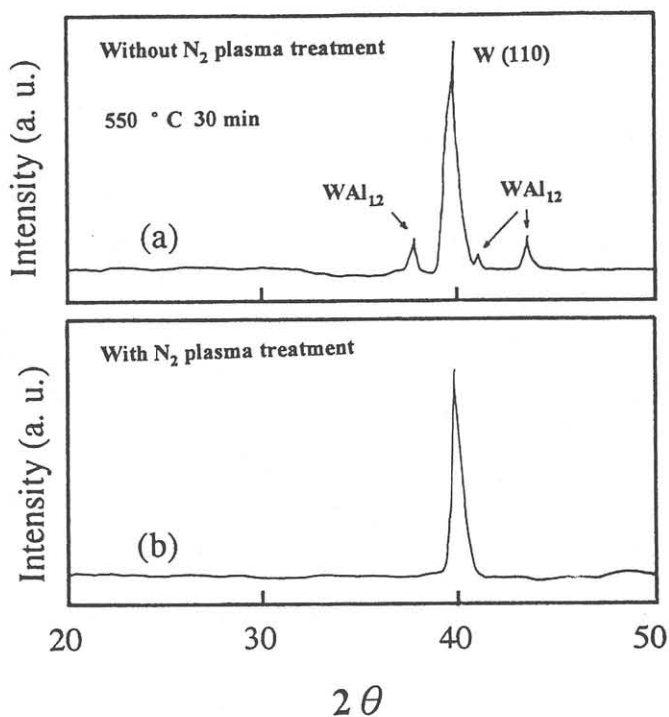


Figure 4 X-ray diffraction patterns of the 550 °C annealed Al/W/Si sample (a) without , and (b) with N<sub>2</sub> plasma treatment.

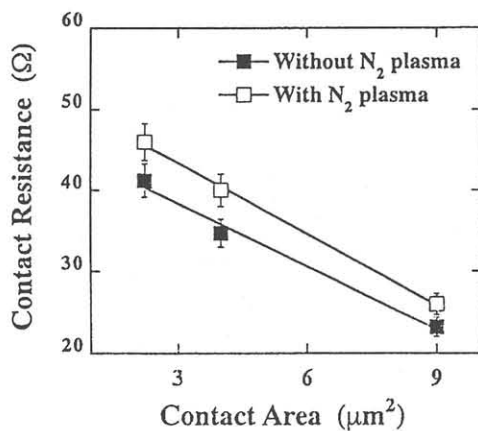


Figure 6 Contact resistance vs. contact area for the Al/W/p<sup>+</sup>n diodes with and without N<sub>2</sub> plasma treatment.

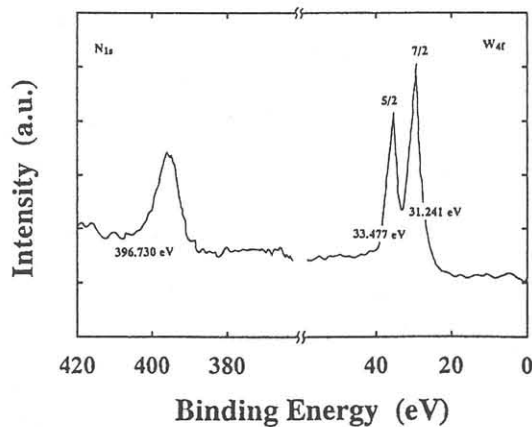


Figure 8 XPS spectrum of the Al/W/Si multilayers with post CVD-W in situ N<sub>2</sub> plasma treatment.