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VHF-PECVD OF Ti/TiN WITH SILANE REDUCTION PROCESS

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ABSTRACT

This paper presents VHF-Plasma Enhanced Chemical Vapor Deposition (VHF-PECVD) of Ti/TiN with silne reduction process, using $TiCl_4$ source. VHF plasma, which is denser than a conventional RF plasma, produces a large number of radicals. Silane reduction process, which supplies silane radicals, more promotes dissociation of Ti-Cl bond than a conventional hydrogen reduction process. therefore, the VHF-PECVD with silane reduction process forms high quality Ti/TiN films, which have low level of Cl content(<0.2 at.%). In result, the resistivity for Ti or TiN is less than $200\,\mu\Omega \cdot$ cm. The surface morphology of Ti film is very smooth. The structure of TiN film is amorphous. Furthermore, excellent step coverage for the films is obtained.

INTRODUCTION

Plasma-Enhanced Chemical Vapor Deposition (PECVD) of Ti or TiN using $TiCl_4$ source is a remarked candidate for contact/barrier film formation in high aspect ratio hole for future ULSIs with 0.25-0.13μm design rule, because the PECVD has the potential for high quality film formation with acceptable conformality. Therefore, many workers have studied about various $TiCl_4$-PECVD methods, such as a conventional RF-PECVD[1-3], ECR-CVD[4-5], and so on, where hydrogen reduction process has been applied for Ti or TiN deposition.

However, there are several problems for the PECVD of Ti or TiN. The most serious one is Clcontaminants which are contained in the film during the deposition, because of reducing device reliability. Cl concentration in the films which are formed by the conventional RF-PECVD is more than 2.0 at .%, resulting that the Cl contaminants cause corrosion of the aluminum interconnects. While, the film with low Cl concentration is formed by ECR-CVD, but its film has poor conformlity. Futher, an ECR-CVD system has a problem that 2.45GHz microwave is not introduced into the reactor when the metal film is deosited on a microwave guide window.

In this work, VHF Plasma-Enhanced Chemical Vapor Deposition (VHF-PECVD) with silane reduction process using $TiCl_4$ source is studied for Ti or TiN formation. VHF plasma, which is denser than a conventional RF plasma[6], produces a large number of radicals. Silane reduction process, whoch supplies silane radicals, promotes dissociation of Ti-Cl bond more than a conventional hydrogen reduction process. These two processes, newly developed, from high quality Ti/TiN film with acceptable conformality. In the follwing sections, VHF-PECVD system, film growth, film characterization results are described.

EXPERIMENTAL PROCEDURE

VHF -PECVD System

A VHF-PECVD system using 60MHz VHF plasma was newly developed on the basis of pallarel plate reactor, which was for a single wafer processing. A schematic diagram of the system is shown in Fig. 1. The 60MHz VHF field generates denser glow discharge plasma than a conventional 13.56MHz RF field. The system is designed so that spark discharge is eliminated in VHF plasma. Electro-Statics Chuck (ESC) is used for sufficient uniformity of substrate temperature. A tank and Mass Flow Controllers (MFC) for $TiCl_4$ precursor are maintained at 75℃ and 80℃, respectively. Then, enough vapor pressure of about 17.3kPa is obtained for stable precursor supply. The rector and a $TiCl_4$ line are also maintained at 80℃ in order to prevent precursor condensation on the wall. The system is evacuated by a turbo molecular pump (TMP) and its base pressure is below 4×10^{-5} Pa.

Film Growth

The Ti or TiN film growth in VHF plasma using $TiCl_4$ based gas system was examined by varying SiH_4 flow rate, where the case of 0 sccm SiH_4 flow rate is the hydrogen reduction process.

Film growth was carried out, as follows. A silicon wafer was introduced into the reactor through a load lock and was set on the base holder heated by a resistance heater. Next, only H_2 gas was fed and 60MHz VHF electric field was applied. Under the VHF plasma, other deposition gases were fed to deposit the films. Deposition process conditions are listed in Table. I, where the condition of 0 sccm silane flow rate means the hydrogen reduction process.

Measurement for Film Characterization

The deposited films were investigated in regard to structure/composition and electrical characteristics. The Cl concentration in the

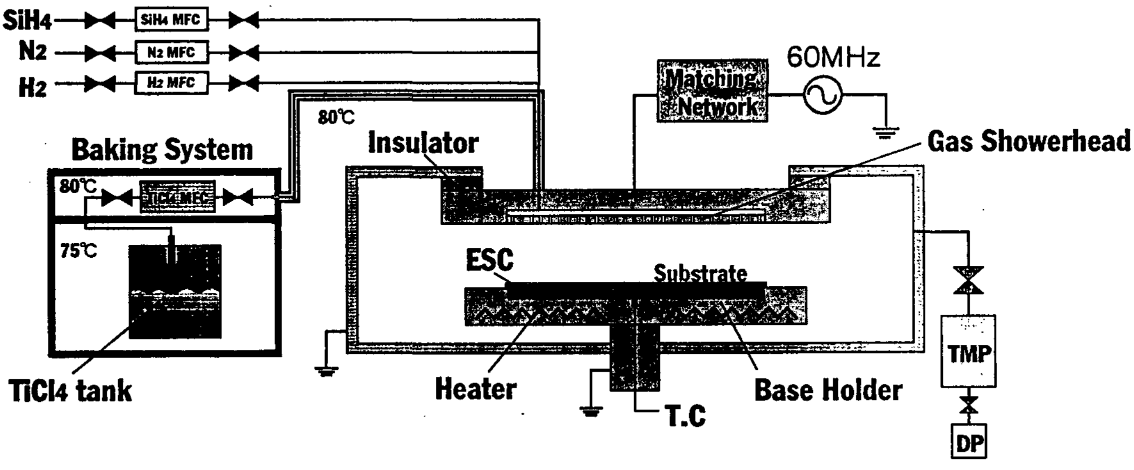


Fig. 1 Shematic diagram of the VHF-PECVD system.

Table. 1 Deposition conditions.

(a) Ti

Sub. Temperature	485℃
VHF Power	500W
$TiCl_4/H_2$	5/500sccm
SiH_4	0-1.5sccm
Pressure	0.12Torr

(b) TiN

Sub. Temperature	485℃
VHF Power	500W
$TiCl_4/H_2$	5/500sccm
N_2	20sccm
SiH_4	0-1.0sccm
Pressure	0.12Torr

film was determined from secondary ion mass spectrosscopy (SIMS). The morphology of the film and step coverage were observed with scanning electron microscopy (SEM). The microstructure of the film was analyzed by X-ray diffractometry. The electrical resistivity was measured by four-point probe method.

RESULTS AND DISCUSSION

Film Growth

The Ti/TiN deposition characteristics with silane reduction process in VHF plasma are described. The dependence of deposition rate of Ti or TiN films on SiH_4 flow rate is shown in Fig. 2 or 3, respectively, where the condition of 0sccm silane flow rate means the hydrogen reduction process. Deposition rate of Ti increases with SiH_4 flow rate and high deposition rate of 15 nm/min is obtained at 1.5sccm SiH_4 flow rate. For this high deposition rate, it is considered that radicals formed from SiH_4 in VHF plasma attack Ti-Cl bond to promote Ti-Ti bond formation. While, deposition rate of TiN dose not change. This result indicates that nitridation process determines the deposition rate of TiN.

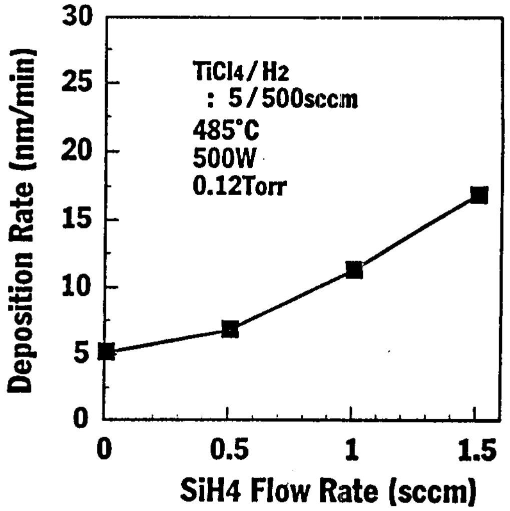


Fig. 2 SiH_4 flow rate dependence of Deposition Rate for Ti.

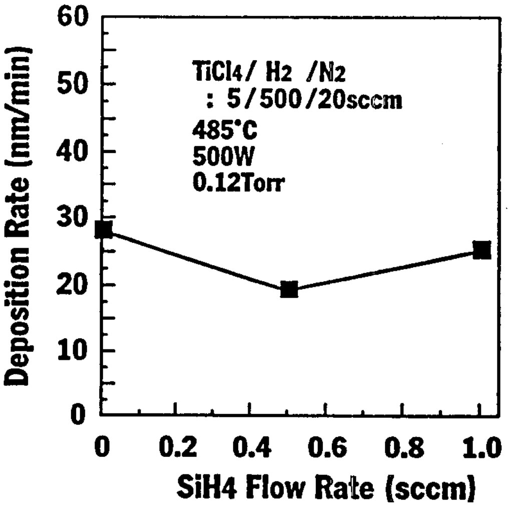


Fig. 3 SiH_4 flow rate dependence of Deposition Rate for TiN.

Film Characterization

In this section, Ti or TiN films are characterized in regard to comparison of the silane

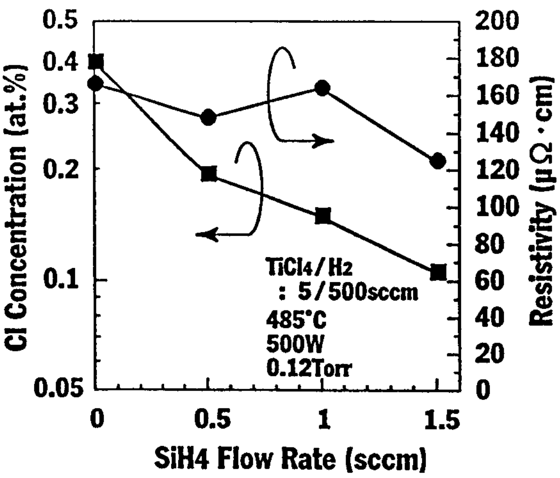


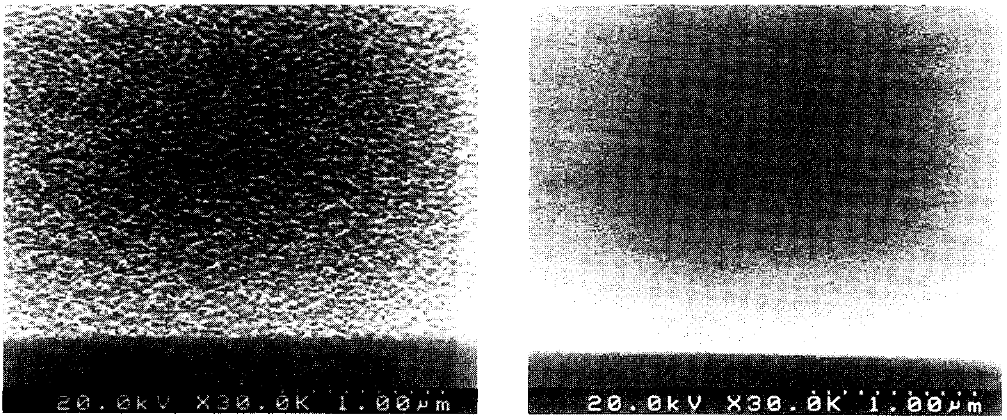
Fig. 4 Relation between CL concentration/resistivity and SiH_4flow rate for Ti films.

reduction process and the hydrogen reduction process in VHF -PECVD.

(1) Ti

Relation between Cl concentration/resisitivity and SiH_4 flow rate is shown in Fig. 4. With SiH_4 flow rate increase up to 1.5 sccm, Cl concentration decreases, while resistivity dose not largely change. Very low Cl concentration of 0.1 at.% is achieved for the film formed under 1.5 sccm SiH_4 flow rate. The mechanism for reducing Cl is explained as follws. In the hydrogen reduction process, radicals formed from H_2 attack Ti-Cl bond to generate desorption species of HCl. While, in the silane reduction process, radicals formed from SiH_4/H_2 attack Ti-Cl bond to generate desortion species of SiClx in addition to HCl. Therefore, the silane reduction process promotes $TiCl_4$ dissociation more than hydrogen reduction, resulting that the silane reduction process allows the renarkable decrease of Cl contaminants.

Morpology, observed with SEM, is sown in Fig. 5(a) for the film formed under hydrogen reduction and in Fig. 5(b) for the film formed under silane reduction. The film formed under hydrogen reduction has rough surface, while the film formed under silane reduction has smooth surface. Rough surface for the film formed under hydrogen reduction is attributed to the rough Ti/Si interfce which is caused by $TiCl_4$ precursor attacking Si substrate surface at the initial stage of film growth . While, under the silane reduc-



(a) (b)

Fig. 5 Surface morphology for Ti films. (a) Hydrogen reduction(SiH_4=0sccm) (b) Silane reduction(SiH_4= 1.0sccm)

(a) (b)

Fig. 6 Cross-sectional SEM micrograph for Ti film formed under 1.0sccm SiH_4 flow rate. (bottom coverage : 50% for ϕ0.4×1.0μm hole)

tion process the silane radicals prevent the $TiCl_4$ precursor from attacking the Si surface. Therefore, the smooth surface of the Ti film is obtained under the silane reduction process.

Step coverage of the Ti film formed under silane reduction is shown in Fig. 6. The hole size is 0.4 μm in diameter and the aspect ratio is 2.4. The bottom coverage value is about 50 % and the side of the hole is sufficiently covered with the film.

(2) TiN

Relation between Cl concentration /resisitivity and SiH_4 flow rate is shown in Fig. 7. With SiH_4 flow rate increase up to 1.0sccm, Cl concentration decreases remarkably, while resistivity dose not largely change. Very low Cl concentration of 0.2 at% is achieved for the film formed under silane reduction. It is also explained by the mechanism described for the case of Ti. Very low resistivity of 100 μΩ · cm is obtained for the film formed under silane reduction. This low resistivity is achieved by very low level of Cl contaminants.

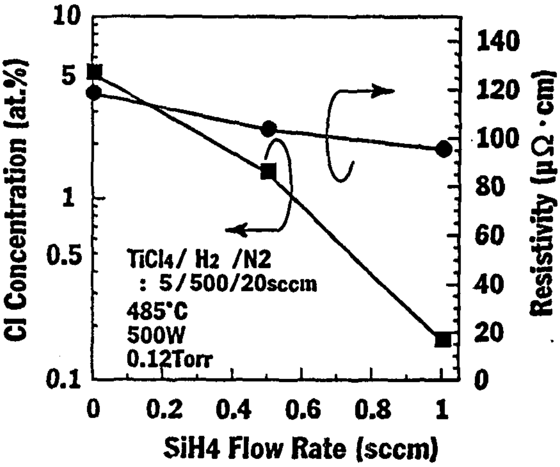
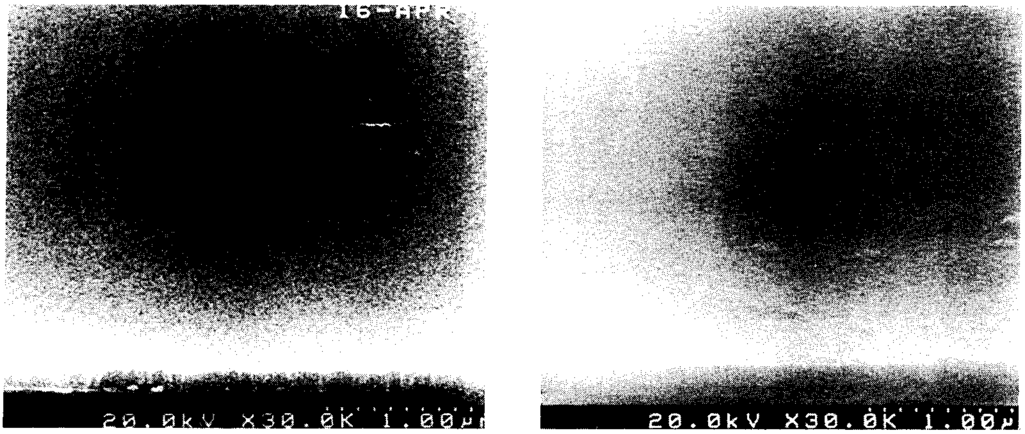


Fig. 7 Relation between Cl concentration/resistivity and SiH_4 flow rate for TiN films.



(a) (b)

Fig. 8 Surface morphology for TiN films. (a) Hydrogen reduction(SiH_4=0sccm)
(b) Silane reduction(SiH_4=1.0sccm)

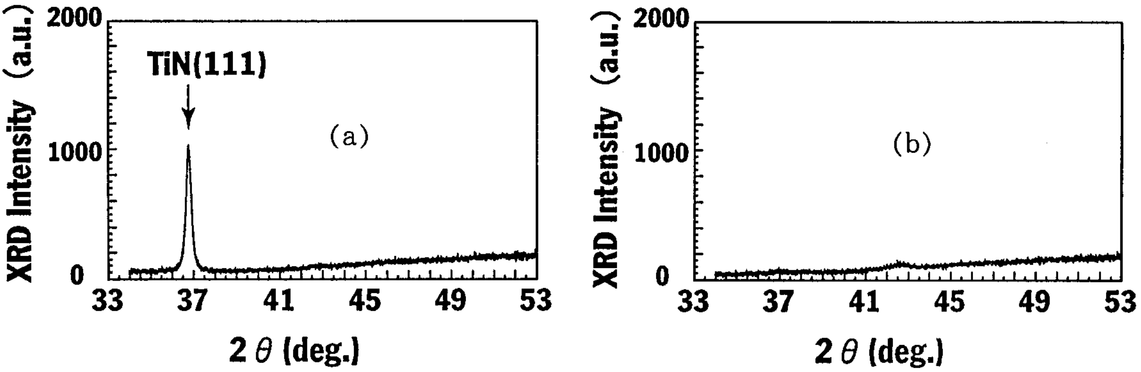


Fig. 9 X-ray diffraction patterns for TiN films. (a) Hydrogen reduction(SiH_4=0sccm)
(b) Silane reduction(SiH_4=1.0sccm)

Morphology for the films is shown in Fig. 8. Fine columnar structure is observed for the film formed under hydrogen reduction in Fig. 8(a). While, smoth surface and amorphous microtexture are observed for the film formed under silane reduction, as shown in Fig. 8(b). This difference is confirmed by X-ray diffraction patterns result are shown in Fig. 9. The peaks of Tin(111) are observed for the film formed under hydrogen reduction. While, obvious peak is not observed for the film formed under silane reduction.

Step coverage of the TiN film formed under silane reduction is shown in Fig. 10. The hole size is 0.4 µm in diameter and the aspect ratio is 2.4. The bottom coverage vlue is about 70% and the side of the hole is sufficiently covered with the film.

CONCLUSION

VHF Plasma-Enhanced Chemical Vapor Deposition of Ti/TiN with silane reduction forms high quality Ti/TiN films from $TiCl_4$

chemistry . Cl concentration in the films is 0.1 at.% for Ti and 0.2 at.% for TiN. Resistivities of the films is 130$\mu\Omega \cdot$cm for Ti and 100$\mu\Omega \cdot$cm for TiN. The surface morphology for Ti film is very smooth and the structure for TiN film is amorphous. Further, the step coverage for the hole is excellent. These results show that this technology is applicable to future ULSI fabrication.

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