

Preparation of TiN Films by ECR Plasma CVD

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TiN film is used in the ultra large scale integrated circuit (ULSI) process as a diffusion barrier. Conventional TiN films are deposited by reactive sputtering or by rapid thermal nitridation (RTN) of sputtered titanium layers. Our research group has developed a new ECR (Electron Cyclotron Resonance) plasma CVD (Chemical Vapor Deposition) system capable of depositing metal films. By using this system, TiN films were prepared using TiCl_4 and N_2 as material gases. It was proven that the films have many advantages: low resistivity, high barrier property, thick deposition on bottom of high aspect ratio's hole and low chlorine concentration in comparison with LPCVD-TiN film.

INTRODUCTION

As current ULSI dimensions approach submicron sizes, it becomes more difficult to achieve reliable interconnection. Especially, electrical properties of contact holes are not reliable due to a poor step coverage of the sputtering techniques. To solve this problem, TiN by LPCVD with TiCl_4 and NH_3 as material gases has been studied¹⁾⁻⁵⁾. LPCVD-TiN has conformal step coverage. However, it is known that TiCl_4 and NH_3 easily form complexes (NH_4Cl etc.) in gas phase at room temperature, and the gas phase reaction generates the precipitation of a yellow powder^{5,6)}. In addition to it, LPCVD-TiN contains a few percents of chlorine, thereby giving a high film resistivity.

An ECR plasma CVD is of great interest to many engineers and has been widely studied⁷⁾⁻¹⁰⁾. However, reports of metal deposition with the ECR plasma CVD method have not been published. In the case of conductive films deposition, it is difficult to maintain a continuous ECR plasma discharge. Because microwaves are reflected or absorbed by the conductive films deposited on the microwave window. Thus our research group developed a new ECR plasma CVD system, which enables us to deposit the conductive films such as metal¹¹⁾.

In this paper, the ECR plasma CVD system developed for conductive film deposition is shown, and characteristics of TiN films deposited by this system are indicated.

EXPERIMENTAL AND RESULTS

Fig.1 shows a diagram of ECR plasma CVD system employed in this work. This concept is nearly equal to that of a conventional ECR plasma CVD. The system consists of two chambers: a plasma chamber and a reaction chamber. The plasma chamber, connected with rectangular waveguide, works as a microwave cavity resonator (TE_{113}). 2.45GHz microwaves are introduced into the plasma chamber through a window.

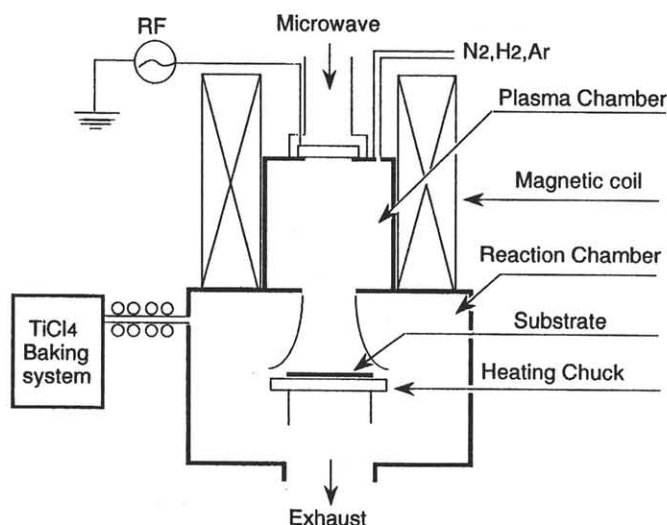


Fig.1 Diagram of ECR plasma CVD system

A magnetic coil is set around the plasma chamber and the magnetic flux density is controlled to be 875 Gauss in order to satisfy the ECR condition. A divergent magnetic field extracts the plasma from the plasma chamber to the reaction chamber.

In order to prevent deposition of the film on the microwave window, we apply RF bias to the window. Then the film will be sputtered and removed, and thereby the ECR plasma discharge could be maintained. TiCl_4 is introduced into a reaction chamber by using a baking system. Hydrogen, nitrogen and argon gases are introduced into plasma chamber. The substrate is heated with the resistance heating chuck. The substrate temperature was controlled with a thermocouple mounted inside the chuck.

Film thickness was determined from cross-sectional SEM photographs. The resistivity of films deposited without annealing was measured by a four-point probe method. Chlorine concentration in the film was measured by energy dispersive X-ray spectroscopy (EDX) and inductively coupled plasma mass spectrometry (ICP-MS).

The total pressure was measured with a MKS baratron gauge.

All of the experiments reported were carried out with 15sccm N_2 , 50sccm H_2 and 43sccm Ar. The substrate temperature was kept at 540°C.

Fig.2 shows dependence of deposition characteristics (deposition rate and film resistivity) on microwave power. The film resistivity is decreasing with increase in the microwave power. Film prepared with 2.8kW microwave power and 10sccm TiCl_4 has a low resistivity of $40\mu\Omega\text{cm}$.

The deposition rate decreases by increasing the microwave power. High powered microwave strongly dissociates TiCl_4 , resulted in increasing etching effect by dissociated chlorine, and apparent deposition rate is decreasing.

EDX spectrum of TiN films prepared with 1.0kW and 2.8kW microwave power are shown in Fig.3(a) and Fig.3(b), respectively. In the case of high powered ECR plasma (for 2.8kW microwave power), the chlorine signal is not detected in Fig.3(b). This indicates that dissociation and reduction of TiCl_4 are enhanced by high powered ECR plasma. Chlorine concentration of the film deposited with 2.8kW microwave power was quantitatively measured by ICP-MS. The chlorine concentration in this film is 0.16 atomic%, which is less than that of the conventional LPCVD-TiN.

Fig.4 shows RBS spectra of Al/TiN/Si (190nm/100nm/Si) contact system before and after heat treatments. The system is stable up to 650°C annealing for 30min and this indicates the high barrier property of TiN deposited by ECR plasma CVD.

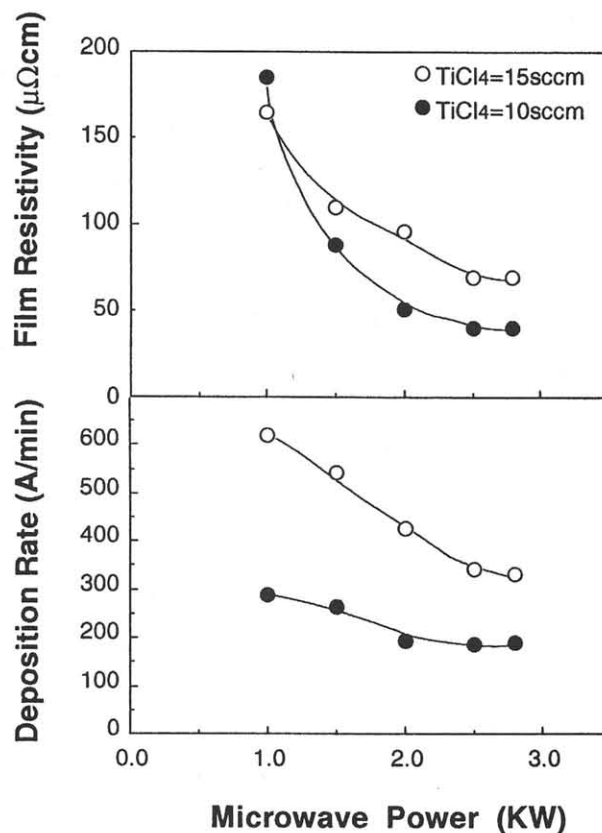
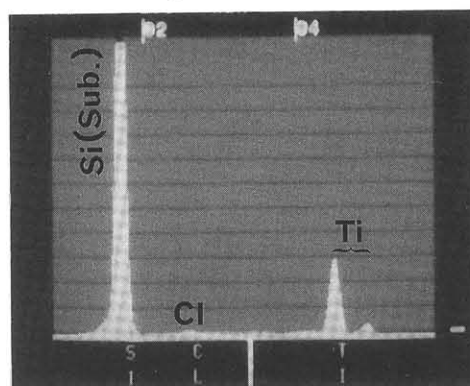
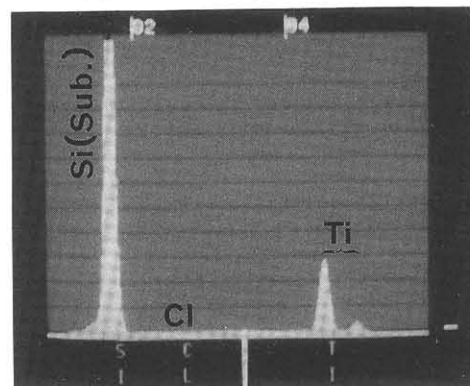


Fig.2 Dependence of deposition characteristics on microwave power



(a) Microwave power 1.0kW



(b) Microwave power 2.8kW

Fig.3 EDX spectra of the films deposited with 1.0kW and 2.8kW of microwave power

SEM photograph of the cross sectional view of TiN deposited on the contact hole is shown in Fig.5. Deposition yield on the bottom of high aspect ratio's hole is higher than that of sputtering process. Step coverage of TiN deposited by ECR plasma CVD differs from that of the conventional LPCVD-TiN. LPCVD-TiN has conformal step coverage, the film thickness on side wall is same as that on bottom or top of contact hole. Therefore, hole diameter becomes narrow and it is serious problem for the next tungsten filling process.

In the case of ECR plasma CVD, film on side wall is thinner than that on the bottom and top of the hole. Tungsten filling is easily carried out.

CONCLUSION

Our research group succeeded in developing an ECR plasma CVD system to deposit conductive films. TiN films deposited by using this system, has many advantages: low resistivity, high barrier property, low chlorine concentration and thick film deposition on the bottom of high aspect ratio's contact hole.

According to these results, ECR plasma CVD process can be useful in ULSI process.

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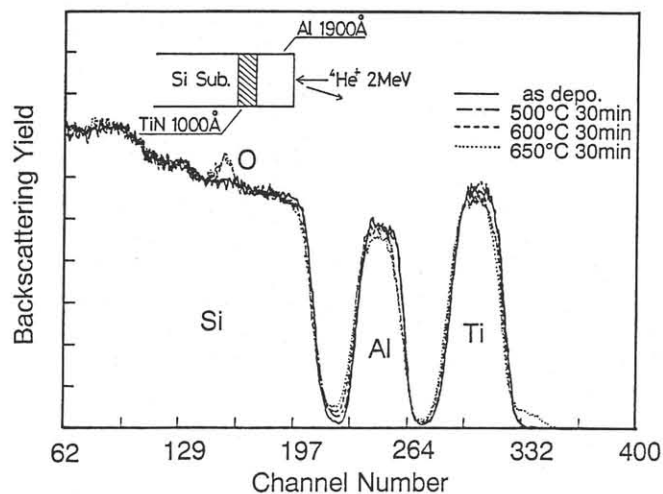


Fig.4 RBS spectra of Al/TiN/Si (190nm/100nm/Si) Contact system before and after heat treatments

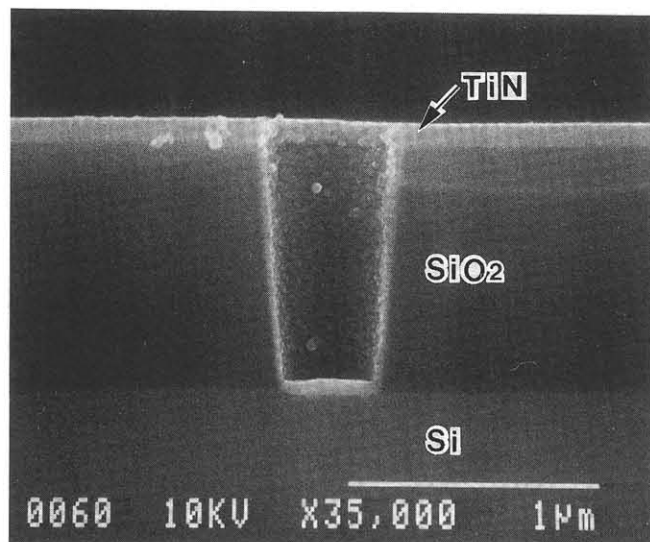


Fig.5 SEM photograph of the cross sectional view of TiN deposited by ECR plasma CVD