Development of Low-resistivity TiN Films using Cat Radical Sources

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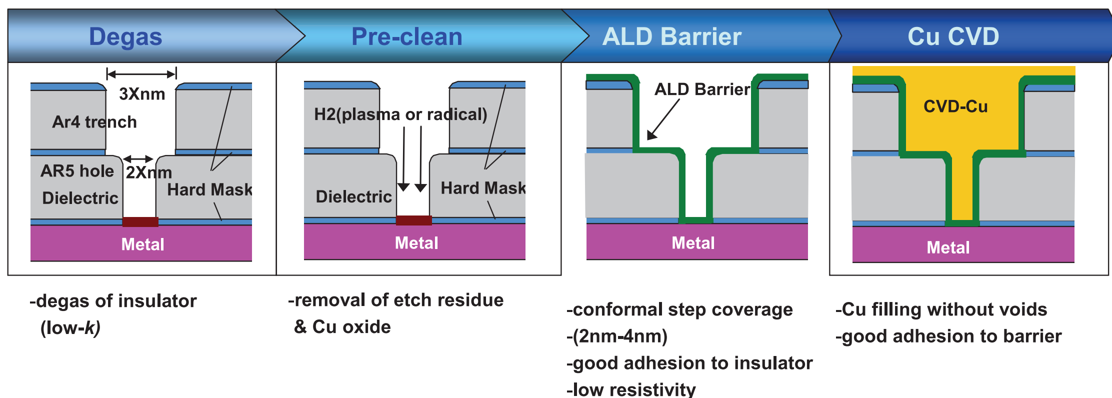
1. Preface

In Cu wiring processes in the 32-nm node generation or later, Cu embedding using the CVD technique as shown below is one of technologies promising to replace currently used plating methods. It requires an integration tool that enables a series of processes in vacuum; degassing of low-k films (mainly for eliminating water), surface washing of under metal films, deposition of Cu barrier films, embedding of trenches and via holes using CVD-Cu films.

The required performance is not only to embed trenches and via holes without voids, but also to satisfy requirements for wiring reliability (SM and EM tests), dust (twenty 0.13 μm particles or less) and throughput (at least 40 wafers per hour). In addition, there is a restriction that the process temperature shall be kept at 300℃ or below in order to prevent Cu from diffusing to dielectric films. To deposit Cu barrier films on such minute holes and trenches, the Third Research Department of the Institute for Semiconductor Technologies is developing ALD-TiN films using the catalytic (Cat) technique. This technique deposits TiN films using the Atomic Layer Deposition (ALD) reaction between a $TiCl_4$ material and NHx (X = 1, 2) radicals dissolved with the Cat technique. This TiN film demonstrated such excellent film characteristics as a resistivity of 80 μΩcm, a chlorine concentration of 1% or less, and a micro hole coverage of 70% at a substrate temperature of 300℃ or below, which is much lower than the temperature in the conventional CVD method. Satisfactory results were also obtained in the adhesion of ALD-TiN films and Cu films.

2. Introduction

Today, TiN films are widely used as barrier films mainly for the aluminum wiring of contact holes of semiconductor devices. They are also studied for use as barrier films for Cu wiring. At present, PVD is the predominant technique for depositing TiN films. But with devices getting smaller and aspect ratios getting larger, studies are being conducted on the deposition of TiN films using the thermal CVD technique and the PECVD technique, which are superior to the PVD technique in coverage performance for holes with high aspect ratios. In some places, the deposition of TiN films in this way has been put into practical use. To obtain high film quality from the thermal CVD technique using $TiCl_4$ as a material, it is necessary to heat substrates to 500℃ or higher to cause the thermal decomposition of $TiCl_4$, but this goes against recent demands for processing advanced devices at lower tempera-



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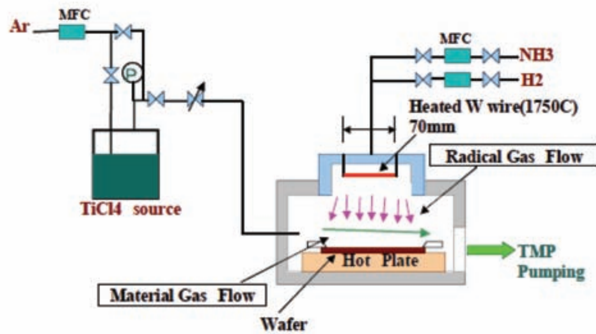

Figure 1　Schematic Diagram of Gas Introduction

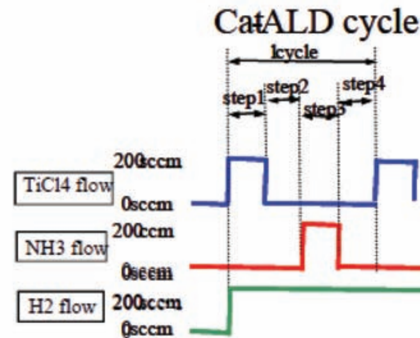

Figure 2　Gas Introduction Sequence

tures.[1,2] On the other hand, the PECVD technique allows for processing at lower temperatures, but it has a problem in that the plasma does not easily enter micro holes and results in poor coverage. For these reasons, we attempted to deposit TiN films using the catalytic (Cat) technique, which has the potential to solve these problems. This technique brings reactive gases into contact with heated catalysts to generate highly reactive radicals.[3] Some of the properties of these radicals is easy reaction with material gases at low temperatures and electroneutrality, so this technique causes less damage than PECVD. Using the Cat technique, we turned the reducing gas NH_3 into radicals, allowed them to react with $TiCl_4$ on substrates, and deposited TiN films at substrate temperatures from 250℃ to 350℃. Then we evaluated film characteristics and obtained the results of a resistivity of 80 $\mu\Omega$cm, a chlorine concentration of 1% or less and a micro hole coverage of 70% at a substrate temperature of 250℃. We also conducted a tape test on a multilayer composed of a 100-nm SiO_2 film, a 10-nm TiN film and a 1-μm PVD-Cu film, and found no delamination at a substrate temperature of 300℃. These results demonstrated excellent adhesion of TiN films to oxide films and upper Cu films.

3.　Experiments

200-mm silicon wafer substrates on which TiN films are deposited are heated to temperatures in a range of 250 to 350℃ on an electrical resistance hot plate. The material gas, $TiCl_4$, is bubbled by the carrier gas, Ar, and then introduced to a chamber. The reactive gases, NH_3 and H_2, are introduced into the chamber from immediately above the substrates, brought into contact with a W catalytic wire heated to 1750℃, turning them into radicals, which then reach the substrates (Figure 1). The W wire, with a diameter of 0.5 mm and a length of about 300 mm, is heated to nearly 1750℃ by applying DC power with a voltage of 12V and a current of 12A. When the W wire is heated, its radiation heat increases the substrate temperature by about 30℃. This temperature rise is taken into consideration in order to correct the substrate temperature. The gas introduction sequence is a 4-step cycle: substrates adsorb $TiCl_4$ in step 1, $TiCl_4$ is degassed in step 2, NH_3 radicals are introduced in step 3 and NH_3 and by-product are degassed in step 4. This cycle is repeated until the desired film thickness is reached (Figure 2). This process resembles the Atomic Layer Deposition (ALD) technique. The ordinary ALD technique has steps with a duration of about 1 second each, but this study set the durations of the steps as step1:step2:step3:step4 (second) = 2:2:10:2 as a core condition. We used SEM for measuring film thicknesses, XPS for film composition, XRD for crystallinity,

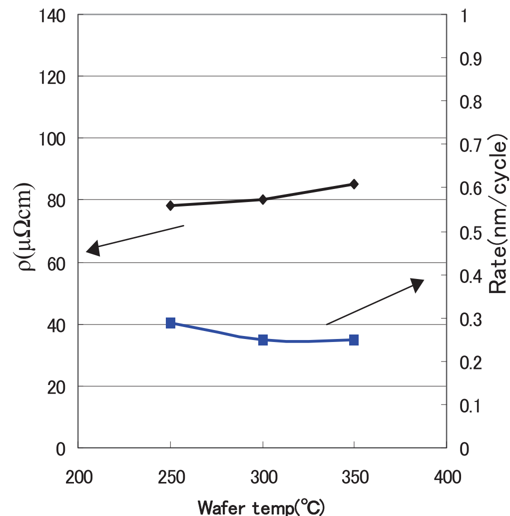

Figure 3　Relationship between Resistivity and Deposition Rate at a Substrate Temperature Varied from 250℃ to 350℃

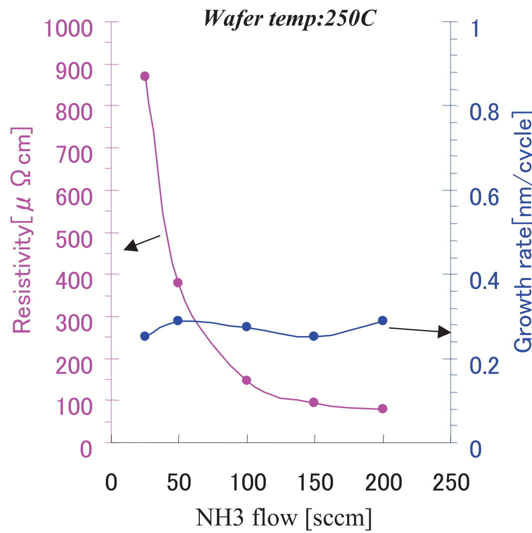

Figure 4　Resistivity and Deposition Rate of a TiN Film versus the NH_3 Flow Rate at a Substrate Temperature of 250℃

and TEM for micro hole coverage. After deposition of TiN films, we introduced substrates into a magnetron DC sputter chamber by vacuum transport and deposited 1000-nm (1-μm) Cu films with a DC power of 5 kW to examine adhesion. Subsequently, we scratched substrate surfaces with a diamond pen to make grid patterns and conducted a tape test.

4.　Results and Consideration

4.1　Basic Film Quality Evaluation

Figure 3 shows the relationship between the resistivity

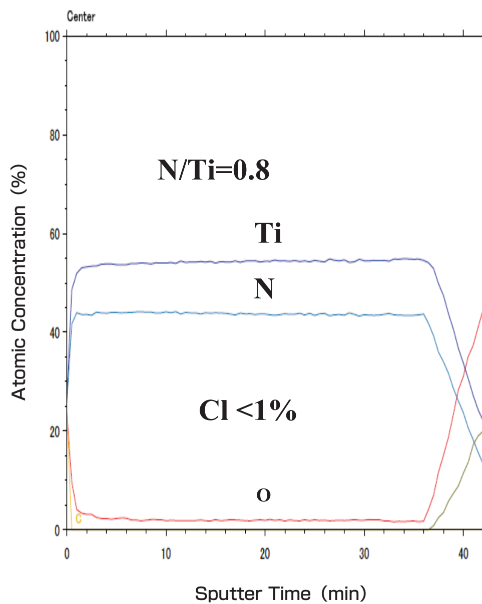

Figure 6　Results of an XPS Composition Analysis of a TiN Film

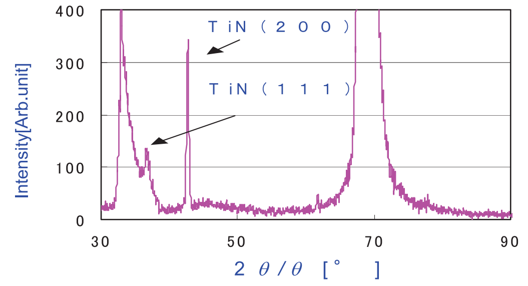

Figure 5　XRD Spectra of a TiN Film

and the deposition rate (nm/cycle) with one cycle fixed to 2s/2s/10s/2s and the substrate temperature varied from 250℃ to 350℃. It shows that the resistivity is almost constant and has no temperature dependence, except that it shows a slight increase at the substrate temperature of 350℃. This indicates that deposition of TiN films mainly depends on the reaction between NH_3 radicals and $TiCl_4$, rather than a thermal reaction depending on the substrate temperature.

Figure 4 shows the resistivity and deposition rate of a TiN film that grew on an oxide film with a varied flow rate of NH_3 at the substrate temperature of 250℃. As the NH_3 flow rate increased, the resistivity decreased. When the flow rate was 200 sccm, the resistivity was 80 μΩcm and the deposition rate was 0.25 nm/cycle. In the ordinary CVD technique, an increase in the NH_3 flow rate generally results in an increase in the proportion of nitrogen in a film and an increase in the resistivity. The reason why an increase in the amount of NH_3 reduces the resistivity is probably that an increase in the amount of NH_3 increases

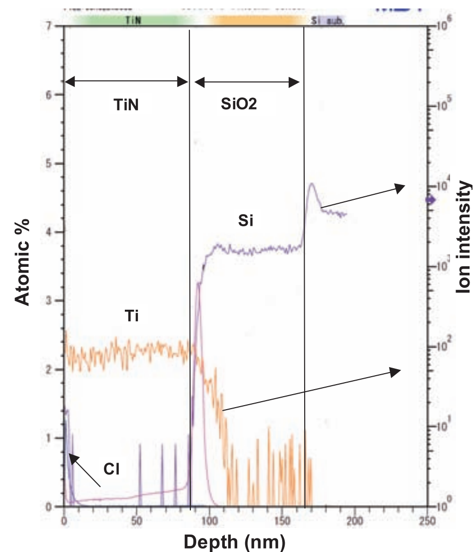

Figure 7　Results of SIMS Analysis of a TiN Film

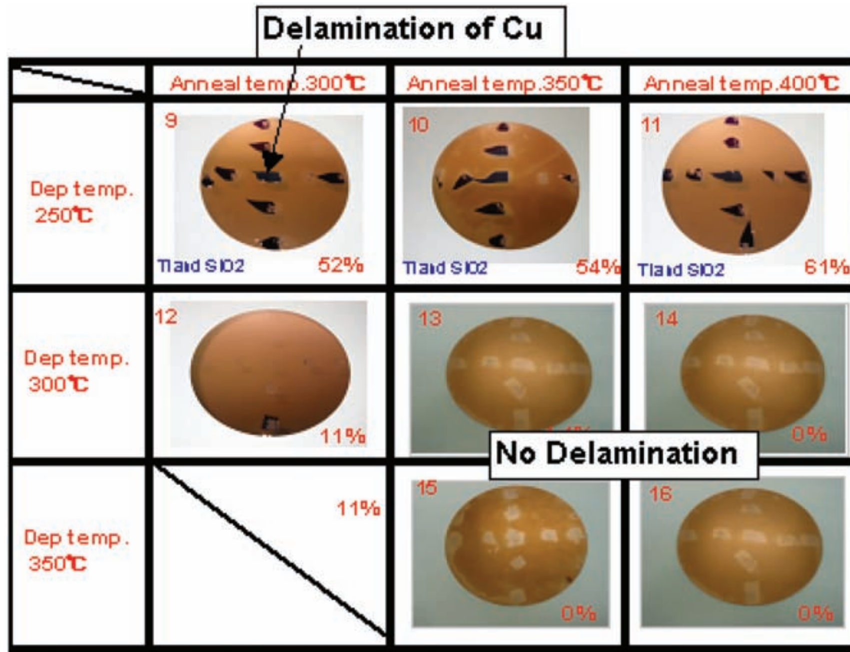

Figure 8 Test results of Adhesion of a TiN Film to a Cu Film

a reduction effect and decreases the chlorine concentration in the film. The reason why the deposition rate was 0.25 nm/cycle, which is about ten times as high as that in the ordinary ALD technique, is thought to be that it takes ten-odd seconds to complete one cycle with this technique, which is much longer than the approximately one second required for the ordinary ALD technique. And in this technique, the deposition of TiN films is affected by CVD reaction (where a gas phase contains both material molecules and reactive gas molecules at the same time), not by complete surface reaction rate control as in the ALD technique.

Figure 5 shows the XRD spectra of this film. It indicates noticeable peaks of TiN <200> and <111> as well as a slight peak of TiN <220>, clearly showing that this is a crystal film. Figure 6 shows the results of an XPS analysis of the composition of this crystal TiN film. The rate of N to Ti is about 0.8, showing that the relative proportion is almost constant within a film thickness of 50 nm. The chlorine (Cl) concentration in the film was lower than the XPS detection limit (1%). However, the results of a SIMS analysis of this film (Figure 7) revealed that about 0.1 to 0.2% of the chlorine remained in the film. There have been reports that the residual chlorine concentration is about several percent in the CVD technique using $TiCl_4$ as a material. The result of this experiment is much lower than the reported level.[1,4)]

4.2 Adhesion to Cu Films

In order to examine adhesion to Cu films, we conducted continuous processing in a vacuum. That processing included deposition of a 10-nm TiN film and a 1000-nm PVD-Cu film on an oxide film wafer and annealing (300℃ to 350℃). Then we scratched wafer surfaces with a diamond pen to make grid patterns and checked for delamination using Scotch tape. Figure 8 tabulates the results of this experiment. These results indicate full adhesion to the 1000-nm Cu film at a deposition temperature of 300℃ or higher and an annealing temperature of 350℃ or higher, except that there was no adhesion between the under oxide film and the TiN film at a deposition temperature of 250℃. Delamination occurred between the TiN film and the oxide film in this case. We believe that more $TiCl_4$ is adsorbed at a lower substrate temperature, $TiCl_4$ cannot be fully reduced by NHx radicals at the initial stage of film deposition and chlorine remains on the interface between the TiN film and the Cu film, thus degrading adhesion.

4.3 Coverage

Using a cross-sectional TEM, we examined the coverage for holes of $\phi 0.18\,\mu m$ and AR = 4 when a TiN film was deposited at a substrate temperature of 300℃. Figures 9a and 9b show cross-sectional TEM images when the NH_3 flow time (duration of step 3) was set to 2 seconds and 10 seconds respectively. The bottom coverage was

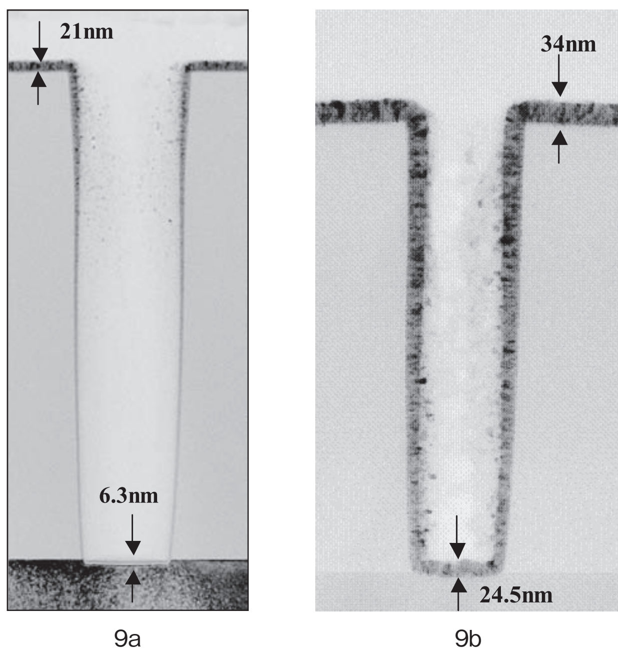

Figure 9 Cross-sectional TEM Images with the NH_3 Flow Time of 2 Seconds (9a) and 10 Seconds (9b)

about 30% with the 2-second flow, and 70% with the 10-second flow. (It was also observed that a columnar crystal structure in the TiN film is clearly seen at the bottom of holes with the 10-second flow, but it is not clear with the 2-second flow.) These results indicate that a certain length of time is required for NH_3 radicals to enter micro holes and deposit a crystalline TiN film.

5. Conclusion

The ALD-TiN films deposited using the Cat technique are crystal films with a resistivity of 80 $\mu\Omega$cm, a residual chlorine concentration of 0.2% or less and a N/Ti of 0.8 at a deposition temperature of 300℃ or lower, showing an excellent film quality. However, the current coverage of 70% is an issue to be addressed in the future, because a coverage of 100% is usually achieved in the ordinary ALD technique. Though good adhesion was observed between ALD-TiN and PVD-Cu films in these experiments, our ultimate goal is to form ALD-TiN and CVD-Cu wires, as mentioned above in the introduction. Also, we need to continue to study the adhesion between ALD-TiN and CVD-Cu films. In terms of mass production, a cycle of ten-odd seconds is considered too long, it needs to be reduced to several seconds. We have many issues, but by solving them we should be able to commercialize TiN films deposited using the Cat technique as barrier films for the Cu or Al wiring of state-of-the-art devices. In addition to these practical improvements, we also need to clarify the elementary steps of radical reaction as a major issue.

This paper is prepared by slightly modifying the outline of the paper we reported at a MRS conference in 2006, titled *Characteristics of very low resistivity TiN barrier film using chemical reaction of Cat radical and* $TiCl_4$.

References

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