Thin Solid Films 519 (2011) 4948–4951

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

Effect of N_2/H_2 plasma treatment on the moisture adsorption of MOCVD–TiN films

J.K. Huang [a], Cheng-Liang Huang [a], Shih-Chieh Chang [b], Yi-Lung Cheng [c], Ying-Lang Wang [b,*]

[a] Department of Electrical Engineering, National Cheng Kung University, Tainan 701, Taiwan, Republic of China
[b] Institute of Lighting and Energy Photonics, National Chiao Tung University, Hsinchu 30050, Taiwan, Republic of China
[c] Department of Electrical Engineering, National Chi-Nan University, Nan-Tou, Taiwan, Republic of China

ARTICLE INFO

Available online 21 January 2011

Keywords:
TiN
MOCVD
Plasma
Aging

ABSTRACT

In the application of contact glue layer for semiconductor devices, a nitrogen/hydrogen (N_2/H_2) plasma treatment is usually used to reduce the amount of C and O impurities of metallorganic chemical vapor deposition titanium nitride (MOCVD–TiN) films. This study found that the sheet resistance of as-deposited MOCVD–TiN film without N_2/H_2 plasma treatment dramatically increased with exposure time due to moisture adsorption. Increasing plasma treatment power and time was able to retard the increase in sheet resistance. From residue gas analysis at 200 °C, it was found that the amount of H_2O outgases from the MOCVD–TiN films decreased with increasing plasma treatment power and time. TEM images reveal that the surface of the MOCVD–TiN films became compact as it received more plasma treatment energy, making it difficult for the external moisture to diffuse into and react with the MOCVD–TiN films.

1. Introduction

Metallorganic chemical vapor deposition titanium nitride (MOCVD–TiN) has been recognized as an excellent barrier and glue layer material in advance metallization for ultra large-scale integrated circuits. It serves as not only a diffusion barrier to protect silicon or underlying metal from tungsten hexafluoride during tungsten chemical vapor deposition (W-CVD) and but also an adhesion layer between dielectrics and W plugs [1–17].

The most common method for depositing TiN film is using terakis-diethyl-amino-titanium (TDMAT) as a precursor in a CVD chamber at ~400 °C [1,2]. However, carbon and hydrogen impurities are always present in the as-deposited TiN film, which leads to the formation of $TiC_xN_yH_z$. Therefore, a post-deposition plasma treatment is needed to remove carbon and hydrogen from the film. The general chemical equations for the deposition process and plasma treatment are respectively as follows [7–11]:

$$\mathrm{Ti(NCH_3)_2)_4} \rightarrow \mathrm{TiC_xN_yH_z} + \mathrm{NH(CH_3)_2} + \mathrm{NH_2CH_3} + \mathrm{NH(CH_2)_2} + \text{other hydrocarbons} \quad (1)$$

$$\mathrm{TiC_xN_yH_z} + \mathrm{N_2} + \mathrm{H_2} \rightarrow \mathrm{TiN} + \mathrm{C_xH_y} + \mathrm{R_2NH} + \text{other byproducts} \quad (2)$$

Plasma treatment lowers the film resistivity and reduces the tendency of oxidation in air. Kröger et al. have reported that most plasma-treated TiN films became crystalline after a short plasma treatment and that the resistivity of the films decreased dramatically [4]. After a long plasma treatment, TiN film became thinner and observable grains extended throughout the entire layer.

It has been reported that post-deposition plasma removed carbon and hydrogen, reducing TiN film resistivity and making the film denser [4–9]. However, little information is available on aging effect of the MOCVD–TiN films. In advanced semiconductor manufacturing, the exposure time of thin MOCVD–TiN films in the atmosphere is a concern for the contact resistance of metal lines. This study investigates the effect of N_2/H_2 plasma treatment on the aging behavior of MOCVD–TiN films. The changes in the sheet resistance and adsorbed moisture of the MOCVD–TiN films are discussed via various plasma treatment conditions and exposure times.

2. Experimental details

In this work, the MOCVD–TiN films were deposited in an Endura™ cluster tool produced by Applied Materials, Inc. For the MOCVD–TiN deposition, the temperature was controlled at 400 ± 2 °C. A blanket (un-patterned) TiN film was deposited on a 100-nm-thick SiO_2/Si wafer. The MOCVD–TiN deposition and subsequent N_2/H_2 plasma treatment were conducted in two repeated cycles. For the N_2/H_2 plasma treatment, the flow rates of H_2 and N_2 gases were 1500 sccm and 1000 sccm, respectively. The process pressures of the TiN deposition and the plasma treatment were at 5 torr and 1.5 torr, respectively. For the aging test, the sample was exposed to the clean-room atmosphere in a wafer cassette from 2 to 690 h. The sheet resistance of blanket TiN films was analyzed using a four-point probe and its thickness was measured using an ellipsometer. The cross-sectional profiles of the MOCVD–TiN films were examined by a

---

* Corresponding author.
E-mail address: ylwang@tsmc.com (Y.-L. Wang).

0040-6090/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.tsf.2011.01.059

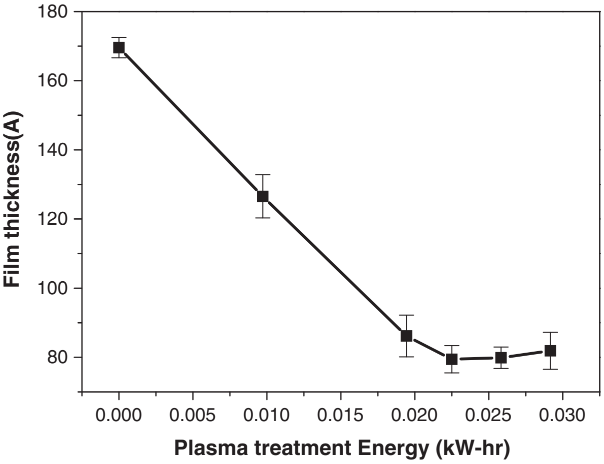

Fig. 1. Effect of plasma treatment energies on the thickness change of the MOCVD–TiN films. The plasma treatment conditions were shown in Table 1.

transmission electron microscope (TEM). The mass spectrum was collected using a residue gas analyzer.

3. Results and discussion

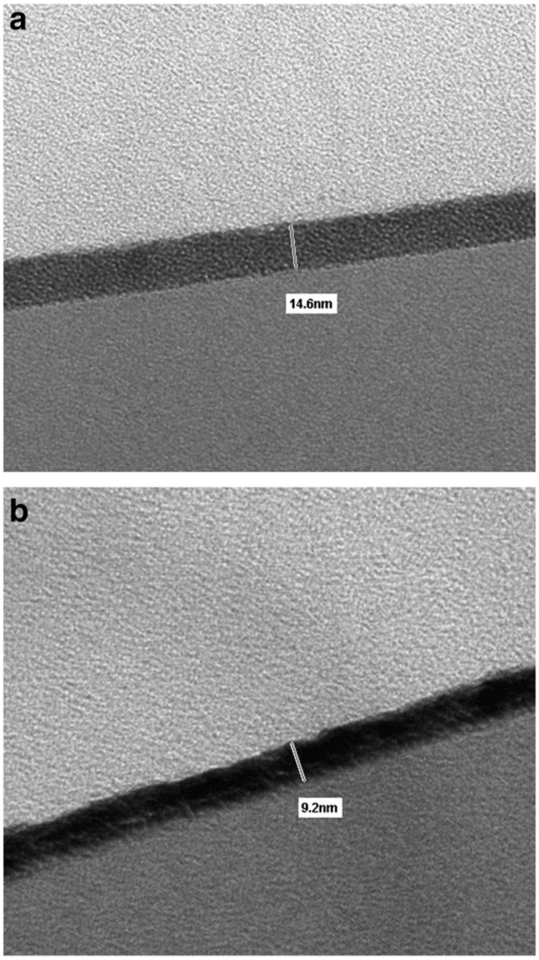

Fig. 2. TEM cross-sectional profiles of (a) as-deposited MOCVD–TiN film without plasma treatment, (b) the MOCVD–TiN film with plasma treatment energy of 0.019 kWh (1750 W/40 s).

Fig. 1 shows the effect of N_2/H_2 plasma-treatment energy on the thickness of the MOCVD–TiN films. Various plasma powers and treatment times were used to treat MOCVD–TiN films. The details of the N_2/H_2 plasma-treatment conditions were listed in Table 1. It was found that the thickness of the MOCVD–TiN films decreased with increasing the plasma treatment energy and it reached to a limited value when the energy was higher than 0.02 kWh. The plasma-treated area became dense and crystalline [4–7]. The TEM images show that after plasma treatment (Fig. 2(b)), the MOCVD–TiN film became denser than that without plasma treatment (Fig. 2(a)). The N_2/H_2 plasma not only physically bombarded the MOCVD–TiN films away from the surface but also chemically reacted with the MOCVD–TiN films. Both chemical reaction and physical bombardment will compact the MOCVD–TiN film. The N_2/H_2 plasma chemically reacted with as-deposited MOCVD–TiN films to remove carbon and hydrogen impurities from the films. The impurities were released as amino-compounds and hydrocarbons after plasma treatment, as shown in Eq. (2). However, physical bombardment will remove the loose part of the MOCVD–TiN film. When plasma treatment energy was higher than 0.02 kWh, the chemical reaction made MOCVD–TiN film compact enough to resist physical bombardment. When the upper MOCVD–TiN film was dense enough, the thickness reduction by physical bombardment effect was reduced. That is why the thickness of the MOCVD–TiN films reached a limited value with increasing plasma treatment energy, as shown in Fig. 1. Fig. 3 shows the effect of N_2/H_2 plasma-treatment energy on the sheet resistance change of the MOCVD–TiN films. The sheet resistance of as-deposited MOCVD–TiN films was ~50,000 Ω/sq. The sheet resistance decreased with increasing plasma treatment energy and reached a limited value when the plasma treatment energy was higher than 0.02 kWh. The result implies that the remained MOCVD–TiN film was nearly treated

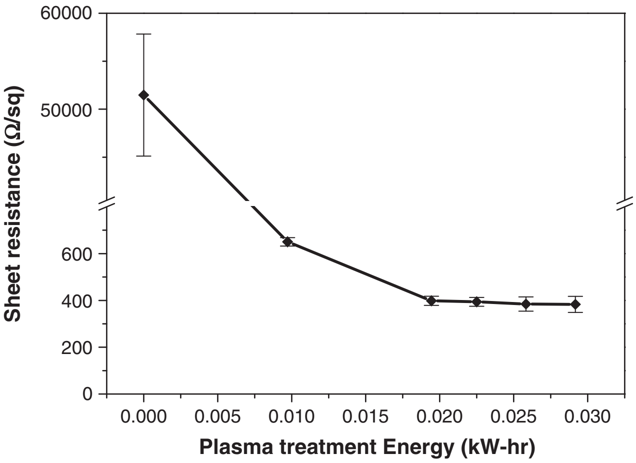

Fig. 3. Effect of plasma treatment energies on the sheet resistance of the MOCVD–TiN films. The plasma treatment conditions were shown in Table 1.

Table 1
List of N_2/H_2 plasma treatment conditions on blanket MOCVD–TiN films. The thickness of blanket MOCVD–TiN films was 17 nm.

Condition	1	2	3	4	5	6
CVD–TiN deposition time	15 s	15 s	15 s	15 s	15 s	15 s
Plasma treatment power	0 W	1750 W	1750 W	1750 W	1550 W	1350 W
Plasma treatment time	0 s	20 s	40 s	60 s	60 s	60 s
Plasma treatment energy	0 kWh	0.01 kWh	0.019 kWh	0.029 kWh	0.026 kWh	0.023 kWh