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Characteristics of TiN Films Deposited by Remote Plasma-Enhanced Atomic Layer Deposition Method

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In this paper, we report a remote plasma-enhanced atomic layer deposition (PEALD) method which shows a relatively wide temperature window compared to the conventional ALD process due to the increased reactivity of reactant gas as well as the increased reactivity of active nitrogen radicals in the plasma process. The remote PEALD TiN films we produced showed significantly lower impurity contents than films deposited by other methods such as plasma-enhanced chemical vapor deposition (CVD), metal-organic CVD or other ALD using the same precursor. TiN films deposited by remote PEALD at 250°C showed a resistivity value as low as approximately 300 μΩ·cm and exhibited excellent conformal deposition with almost above 95% step coverage on a 0.25-μm-wide and 2.5-μm-deep contact hole structure.
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KEYWORDS: remote PEALD, diffusion barrier, TiN, TDMAT

Many researchers have been studying the application of the atomic layer deposition (ALD) technique to the deposition of diffusion barrier films for overcoming the combined problems of the physical vapor deposition (PVD) and chemical vapor deposition (CVD) methods.[1–3] The ALD method has a lot of advantages over other deposition methods such as excellent thickness uniformity with conformal deposition over large substrate areas, low processing temperatures, low impurity contents and complete precise control of film thickness.[4–7] Many ALD researchers have studied the growth of diffusion barrier layers using mainly halide precursors.[6–9] However, the ALD method using halide precursors showed problems such as corrosion due to chlorine contamination, a slow growth rate and a relatively high deposition temperature. To solve these problems, ALD with metal-organic precursors is suggested. However, the diffusion barrier layers deposited with the metal-organic ALD (MOALD) method showed relatively high carbon impurity incorporation. Also, the process window of MOALD is reduced due to the limited choice of precursors and/or reactants.[10)]

Recently, the plasma technique has been suggested to improve the film quality as well as to overcome many problems of the ALD method.[11)] In this study, we built a remote plasma-enhanced ALD (PEALD) system to investigate the characteristics of the diffusion barrier thin films. Remote PEALD is designed to place the substrate outside the plasma region and is expected to reduce the carbon impurity and substrate damage. This paper will present the characteristics of TiN films grown by the remote PEALD system using tetrakis-dimethyl-amino-titanium (TDMAT) precursor and N_2 plasma.

TiN films were deposited on an SiO_2 layer using TDMAT as the Ti precursor and N_2 as the reactant gas. The SiO_2 layer with a thickness of 1000 Å was deposited on a silicon substrate prior to TiN deposition using the thermal oxidation method at 1000°C. Before TiN deposition, the SiO_2 layer was cleaned by dipping in piranha solution ($H_2SO_4 : H_2O_2 = 4 : 1$) for 10 min to remove organic contaminants. Process parameters such as the reaction time, gas flow rate, temperature and plasma power were investigated to optimize the process conditions. TDMAT was delivered from an external reservoir at 45°C and pulsed into the reactor using Ar carrier gas with flow rate of 20 sccm. Ar purge and reactant gas flow rates were fixed at 100 and 70 sccm, respectively. The chemical reaction of TDMAT pulse and N_2 plasma pulse completed one basic cycle in this experiment. Ar purge gas was introduced for the complete separation of the precursor and plasma reactant gases. All of the gas flows were automatically controlled by the aid of a solenoid valve. The sequential process times of TDMAT, Ar-purge, N_2 plasma and Ar-purge were fixed at 5 s each, except the plasma process time of 20 s. TiN films were deposited in the temperature range of 150 to 350°C, and the total pressure was kept constant at 0.1 Torr. A downstream-type remote PEALD reactor with a 13.56 MHz rf power generator was used in this study. The plasma power was fixed at 300 watts.

The resistivity of the TiN films was measured using a four-point probe technique. Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS) were utilized to analyze the chemical composition, impurity contents and chemical bonding structures. The step coverage of the TiN films was investigated using cross-sectional transmission electron microscopy (XTEM).

Figure 1 shows the growth rate and resistivity of TiN films deposited using TDMAT precursor and N_2 remote plasma reactant gas at various temperatures. The TiN films showed a saturated growth region in the temperature range of 200 to 300°C and showed a linear relationship between the film thickness and number of processing cycles as shown in Fig. 1. The film growth rate was constantly maintained independent of deposition temperatures and satisfied the ALD process window condition. This wide temperature window compared to that of the conventional ALD method is believed to be due to the increased reactivity of reactant gas as well as the increased reactivity of active nitrogen radicals in the plasma process. The growth rates increased rapidly as the deposition temperature increased above 300°C due to the self-decomposition of TDMAT which resulted in a CVD-like growth. The resistivity of TiN films is one of the most important factors for metal diffusion barrier application. TiN films processed with nitrogen remote plasma showed resistivity values as low as approximately

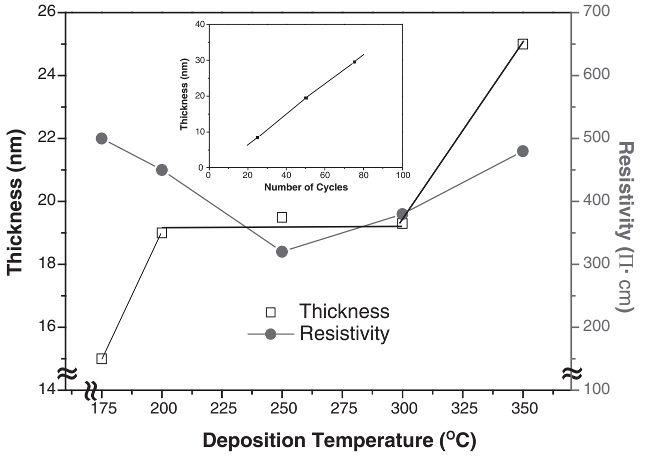
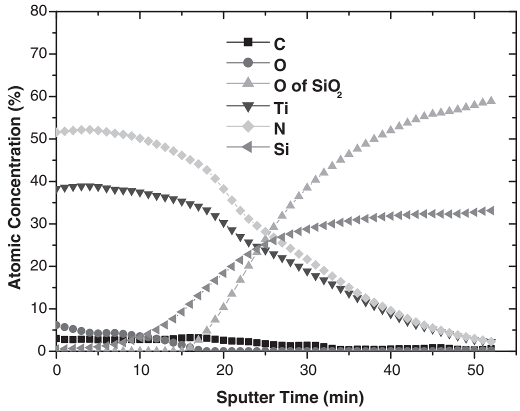


Fig. 1. Growth rate and resistivity of TiN films deposited by remote PEALD technique using TDMAT precursor and nitrogen plasma as a function of deposition temperature. Inset of this figure shows the film thickness as a function of process cycles.

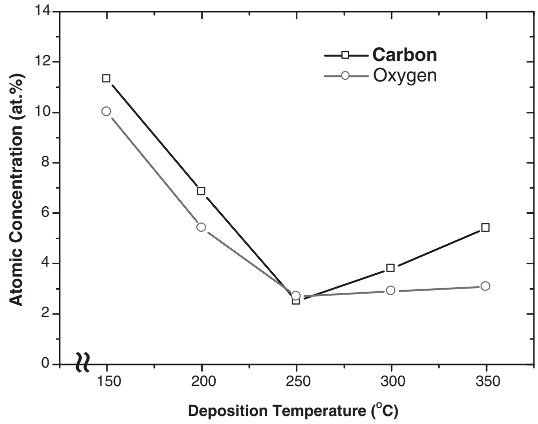
300 μΩ·cm. These values are significantly lower than those of TiN films deposited by conventional metal-organic CVD and other ALD methods using TDMAT precursor.[12,13] The resistivity of TiN films is reported to closely relate to the impurity contents, indicating that the remote PEALD method significantly reduces the impurity contents. Activated nitrogen is considered to play a major role in this plasma process. The good quality of TiN films is due to the effectively broken bond between Ti and the ligand by this activated nitrogen.

The chemical composition and impurity contents of the TiN films were examined by AES and Fig. 2(a) shows the typical AES depth profile of TiN films deposited by the remote PEALD method at 250°C. TiN films showed relatively constant compositional variation and stoichiometric TiN. Carbon and oxygen impurities in TiN films in the ALD process window were below 10 at% as shown in Fig. 2(b). This is approximately one order lower than that of the films deposited by other conventional deposition methods.[12,14] Others reported that TiN films deposited by the conventional ALD method using the same precursor showed carbon and oxygen contents of 14 and 20 at%, respectively.[13] One explanation for these low impurity contents is the increased reactivity of nitrogen gas and/or active nitrogen radicals which efficiently decompose the dimethyl-amino group in the plasma process. Another possibility is the enhanced physical properties, such as the density of the films, due to nitrogen remote plasma which caused reduced impurity incorporation in the films during deposition. In this study, TiN films showed impurity contents of carbon and oxygen as low as approximately 3 and 3.5 at%, respectively.

The resistivity of TiN films was reported to be closely related to the amount of C–H bonding in the films.[12] If the amount of C–H bonding in TiN films is small, the resistivity of the TiN films is decreased. Figure 3 shows the high-resolution XPS spectrum of carbon impurity in TiN films deposited by the remote PEALD method. The calculated amounts of Ti–C and C–H bondings of carbon impurity in the TiN films were approximately 97 and 3%, respectively. This relatively lows amount of C–H bonding and reduced carbon impurity in remote PEALD TiN films are believed to be related directly to the low resistivity of the TiN films.



(a)



(b)

Fig. 2. AES depth profile (a) and impurity contents (b) of TiN films deposited by remote PEALD method using TDMAT precursor and nitrogen plasma.

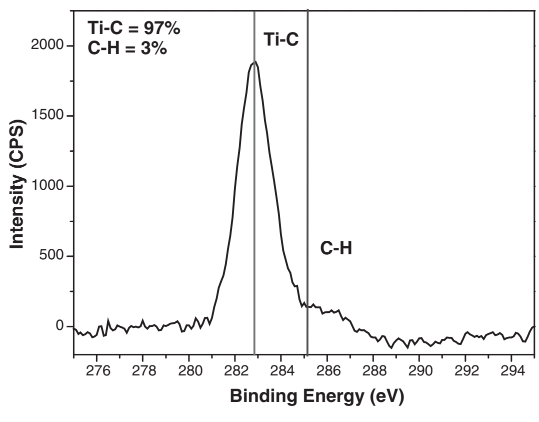


Fig. 3. High-resolution XPS spectrum of carbon in TiN film deposited by remote PEALD method using TDMAT precursor and nitrogen plasma at 250°C.

Figure 4 shows the XTEM image of a TiN film on contact holes approximately 0.25 μm wide and 2.5 μm deep. The TiN film showed excellent conformal deposition with almost above 95% step coverage. This conformal coverage of TiN also indicates the uniform radical density over the substrate which results in uniform surface growth and self-limited reaction.

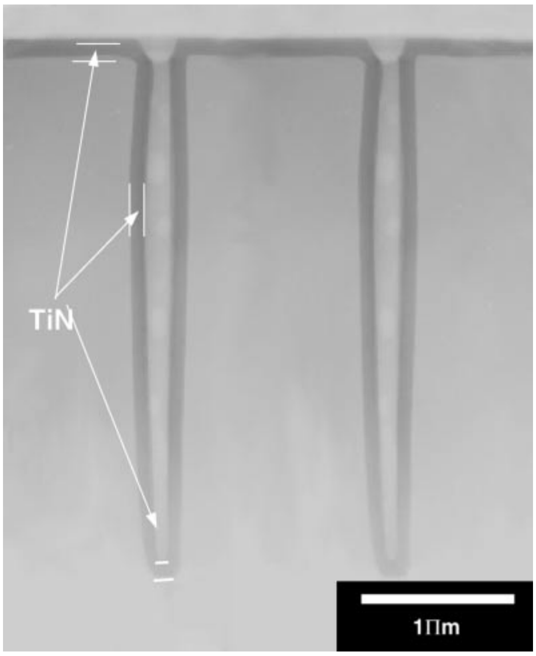


Fig. 4. XTEM image of TiN film deposited by remote PEALD method on contact hole approximately 0.25 μm wide and 2.5 μm deep.

In summary, TiN films were successfully deposited by the remote PEALD method using TDMAT precursor and nitrogen plasma. The TiN films showed a saturated growth region in the temperature range of 200 to 300°C. This wide ALD temperature window compared with that of the conventional ALD process is due to the increased reactivity of reactant gas as well as the increased reactivity of active nitrogen radicals in the plasma process. Remote PEALD TiN films showed much lower impurity contents than films deposited by other methods such as plasma-enhanced CVD, MOCVD or other ALD using the same precursor. The TiN films showed resistivity values as low as approximately 300 μΩ·cm and excellent conformal deposition with almost above 95% step coverage.

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