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Characterization of CVD-TiN Films Prepared with Metalorganic Source

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This paper investigates the structural and electrical properties of TiN films prepared by metalorganic chemical vapor deposition (MOCVD) using a mixture of tetradimethylamino-titanium ($\text{Ti}(\text{N}(\text{CH}_3)_2)_4$) and NH_3 gases. The deposited films changed from a metallic gray to a gold color at a substrate temperature of 300–580°C. The film resistivity decreases with increasing substrate temperature to $8.4 \times 10^2 \mu\Omega \cdot \text{cm}$ at 580°C. The preferred orientation was (111) at temperatures over 400°C.

KEYWORDS: MOCVD, TiN, resistivity, XPS, X-ray diffraction, SEM

§1. Introduction

The shrinking of LSI has caused problems regarding the contact metal and the Si substrate. In particular, interaction between Al and Si causes increasing contact resistance and junction destruction. Therefore, it is necessary to use a diffusion barrier for submicron contact holes.

Some researchers have reported that titanium nitride is one of the most attractive diffusion barrier materials because of its stability to heat treatment.^{1,2)} In addition, its bulk resistivity is one of the lowest for a transition element of nitride. Most of the work has used the technique of reactive sputtering using a Ti target in N_2 and Ar.^{1,3)} However, physical vapor deposition, including sputtering, cannot form the conformal step coverage for the high aspect-ratio holes required for ULSI.

On the other hand, chemical vapor deposition (CVD) gives conformal step coverage because reactants or reactive intermediates migrate rapidly along the surface before reacting. Some groups have used metal-halogen compounds such as a mixture of titaniumtetrachloride and ammonium or nitrogen gas.⁴⁻⁶⁾ However, the resulting films contained a small amount of chloride impurity. In addition, with NH_3 gas, the reaction byproduct, ammonium chloride, is responsible for contamination.⁶⁾

This study presents a new attempt to prepare CVD TiN films using a mixture of the metalorganic source $\text{Ti}(\text{N}(\text{CH}_3)_2)_4$ and NH_3 gases. The dependence of structural and electrical properties on the substrate temperature and gas composition was studied.

§2. Experimental Procedure

A schematic diagram of the experimental apparatus is shown in Fig. 1. The deposition reactor was of the cold-wall type. The substrate was heated by the halogen lamp through the bottom quartz window of the reactor.

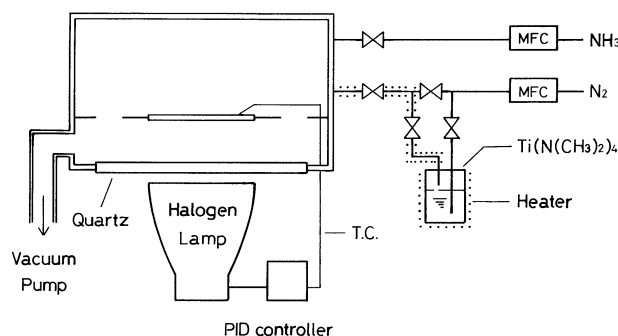


Fig. 1. Schematic diagram of the experimental apparatus.

Deposition temperatures ranged from 300°C to 580°C, and were controlled to within 1% by a Parallel Integrated Differential (PID). Oriented (100) n-type Si wafers and thermally grown silicon dioxide substrate were used. The tetradimethylamino-titanium ($\text{Ti}(\text{N}(\text{CH}_3)_2)_4$) was kept in a cylinder at 37°C, through which nitrogen carrier gas was bubbled. This source is a liquid at room temperature and has a vapor pressure of 0.01 mmHg at 37°C. NH_3 was also used as a reactive gas. These sources were fed into the reactor through separate inlets. The deposition pressure was maintained at 0.3 Torr after the reactor was evacuated to below 3×10^{-6} Torr. The nitrogen carrier gas flow rate and NH_3 gas flow rate were fixed at 2 sccm and 10 sccm, respectively.

Structural and electrical properties were investigated using X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), scanning electron microscope (SEM), and the four-point probe method.

§3. Results and Discussion

Figure 2 shows the XPS spectra of the Ti_{2p} region and the N_{1s} region, comparing that for CVD using a metalorganic source to that for sputtering. In the CVD, the film was deposited at 500°C, and the deposition rate was 60 Å/min. The surfaces analyzed were etched with 2

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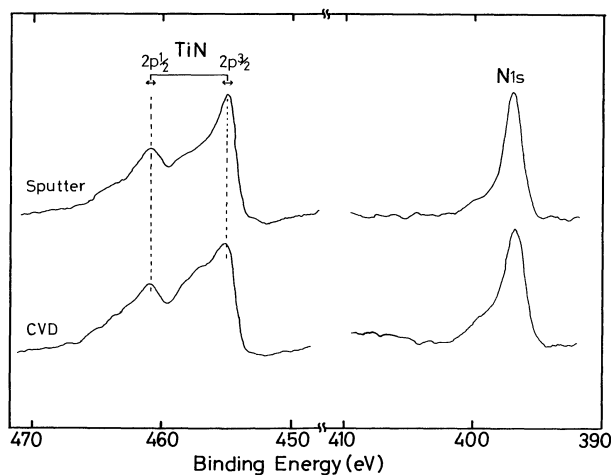


Fig. 2. The XPS spectra of the Ti_{2p} region and N_{1s} region from the CVD process and the sputtering.

keV Ar-ion sputtering for 2 minutes. The Ti_{2p} spectrum of the CVD process has a typical satellite structure with $Ti_{2p}^{1/2}$ and $Ti_{2p}^{3/2}$ peaks at binding energies of about 461 eV and 455 eV, respectively. Both values agree with reported chemical shifts from Ti metal peaks to bond to the N.⁷⁻⁹⁾ In addition, the Ti_{2p} and N_{1s} peaks of the CVD process are similar to those for sputtering. However, the Ti_{2p} spectrum for CVD contained another peak which was not found in the spectrum for sputtering. It was observed at 2.5 eV higher than the maximum peak, and which corresponds to the energy of titanium dioxide.⁹⁾

The XPS spectra of the C_{1s} region deposited at 400°C and 580°C are shown in Fig. 3. The spectra at 400°C has three peaks. The largest, at 285 eV, represents hydrocarbons. The small peak at 282 eV corresponds to the energy of TiC.¹⁰⁾ A shoulder hydrocarbon peak at 286 eV corresponds to methylamine.¹¹⁾ These results indicate that a small amount of TiC and unreactive sources is contained in the film contains. For the film deposited at 580°C, carbon inclusion is noticeably reduced, as shown in Fig. 3; the shoulder at 286 eV disappears and the peaks at 282 eV and 285 eV are also reduced.

The texture and color of films at different substrate temperatures are shown in Table I. The X-ray diffraction pattern for films deposited at more than 400°C has a NaCl-type structure, oriented (111) texture and increases monotonically with the deposition temperature. While the (100) texture was observed at over 500°C, the amount was much smaller than the amount of (111) texture at 580°C. Debye-Scherrer's formula shows the grain size of the (111) crystalline component to be about 300 Å. The film color changed from a metallic gray to a gold color with rising deposition temperature. It is considered that the film deposited at 300°C is nitrogen-poor and amorphous, but at 580°C is stoichiometrically crystalline.¹²⁾ This can be explained by the enhanced decomposition of NH_3 gas at higher deposition temperatures and the increased nitridation.

The resistivity of the film as a function of the deposition temperature is shown in Fig. 4. The resistivity decreases with increasing substrate temperature, and the

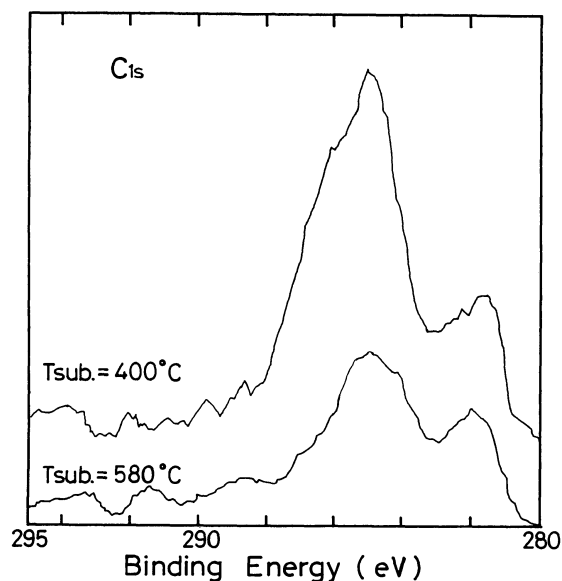


Fig. 3. The XPS spectra of the C_{1s} region from CVD-TiN.

Table I. The texture and color of CVD-TiN films.

T_{sub} (°C)	Color	Texture
300	Gray	amorphous
400	Brown Black	(111)
500	Brown	(111) (100)
550	Light Brown	(111) (100)
580	Gold	(111) (100)

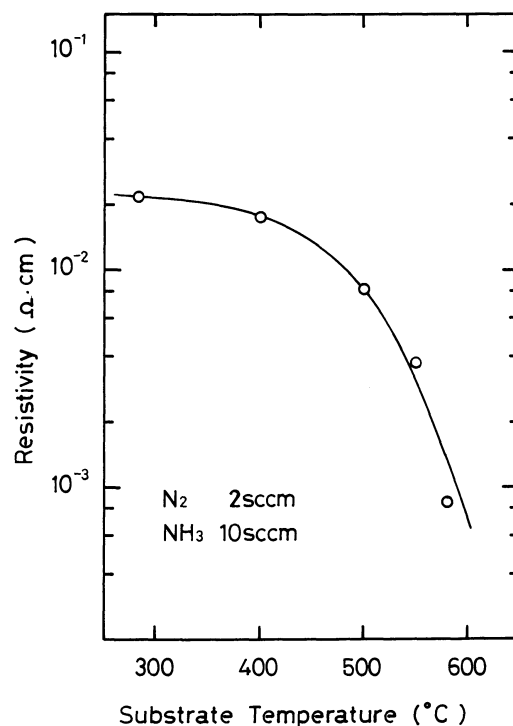


Fig. 4. Film resistivity film as a function of deposition temperature.

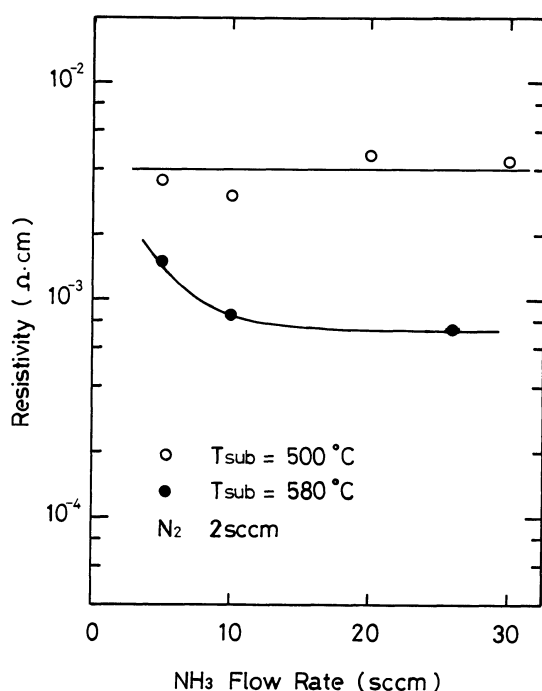


Fig. 5. Film resistivity as a function of the NH₃ flow rate.

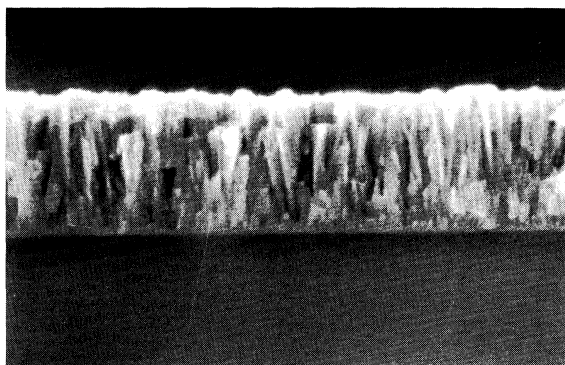


Fig. 6. SEM picture of the cross section of CVD-TiN.

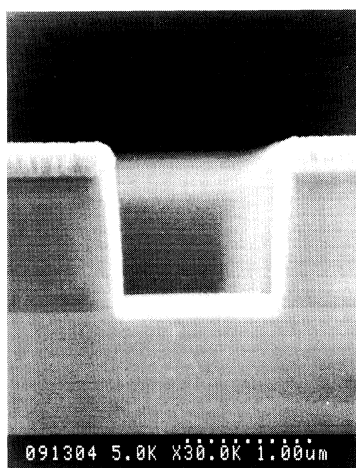


Fig. 7. SEM picture of the step coverage with CVD-TiN.

resistivity of the film deposited at 580°C was about $8.4 \times 10^2 \mu\Omega \cdot \text{cm}$. From the analysis of XPS and X-ray diffraction, it is presumed that the decrease in resistivity is due to the structural changes and the reduction of carbon.

The resistivity of the film as a function of the NH₃ flow rate at 500°C and 580°C is shown in Fig. 5. The source carrier gas flow rate was fixed at 2 sccm. The resistivity in the film deposited at 500°C has no marked dependence on NH₃ gas flow rate. However, with the film deposited at 580°C, the resistivity decreased with increasing NH₃ flow rate. This result also suggests that the decomposition of NH₃ gas is enhanced at 580°C, encouraging nitridation.

An SEM picture of the cross-sectional view of the CVD-TiN film at 500°C is shown in Fig. 6. The film consists of dense columnar grains. It has been reported that polycrystalline TiN appears to oxidize preferentially at the grain boundaries.⁸⁾ The Ti_{2p} shoulder in the XPS spectra is considered to be due to oxide at the grain boundaries. An SEM picture of the step coverage is shown in Fig. 7. The extent of step coverage was evaluated with a 1 μm line-and-space pattern on PSG deposited on the Si wafer. This figure shows that the CVD-TiN film has good conformal step coverage.

§4. Conclusions

CVD-TiN films were deposited from a Ti(N(CH₃)₂)₄-NH₃ gas mixture, and properties of the films were investigated. The results are as follows.

The XPS spectra of Ti_{2p} and N_{1s} for CVD-TiN were similar to those for sputter-TiN. The resistivity of the film deposited at 580°C was $8.4 \times 10^2 \mu\Omega \cdot \text{cm}$, and its color was gold. The structure of the film was columnar grains, and its primary texture was (111). However, the film contained small amounts of carbon impurity, especially at low deposition temperatures.

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