Oxidation resistance of atomic-layer deposited TiN films on thermal SiO_2

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ABSTRACT

In this study, an atomic-layer deposition system was used to deposit TiN films on thermal SiO_2 substrates by means of sequential pulses of $TiCl_4$ and NH_3. The effects of deposition temperature on TiN growth rate, film compositions, and oxidation properties were investigated. The results show that the growth rate is about 0.3 nm per deposition cycle and almost independent of the deposition temperature in the range of 300-500^{o}C. The oxidation resistance, however, highly depends on the deposition temperature. The XRD patterns show that the TiN films deposited at 300^{o}C were oxidized and became TiO_2 compound after 1 hr annealing at 500^{o}C in O2 atmosphere, whereas the films deposited at 500^{o}C still had good conductivity and no TiO_2 diffraction peaks were found.

INTRODUCTION

Titanium nitride (TiN) films are widely used as adhesion layers and diffusion barriers for W, Al, and Cu metallization. One of the most popular deposition methods for TiN films is reactive sputtering. However, the reactive sputtering method is getting insufficient as the device dimensions shrink into nano-scale regime. Atomic-layer deposition (ALD) is one of the most promising deposition methods for nanoscale integrated circuits (IC) due to its excellent uniformity, accurate thickness control, low deposition temperature, and almost 100% step coverage [1,2]. Therefore, atomic-layer deposited TiN is getting attraction for diffusion barrier in future high-density dynamic and ferroelectric random access memory devices [3]. The chemical stability of barrier films is essential to prevent oxidation as processing high-k oxides. The oxidation resistance of TiN films grown by reactive sputtering has been found to be related to the process parameters [4,5]. In this study, the oxidation resistance of TiN films grown by ALD was investigated.

EXPERIMENTAL DETAILS

TiN films were grown on SiO_2/p-Si substrates at deposition temperatures of 300-500^{o}C in a

hot-wall ALD system. The precursors of $TiCl_4$ and NH_3 were alternatively introduced into the ALD chamber through time controlled solenoid valves. The time for each step is 3, 2, 5, 2.5, 2.5, and 5 s respectively for $TiCl_4$ reactant, pump-down, Ar purge, NH_3 reactant, pump-down, and Ar purge steps. 1000 cycles in total were conducted for each sample. The flow rates of NH_3 and Ar, determined by the gas flow meters, were 6.4 cc/pulse and 5.2 cc/pulse respectively. The flow rate of $TiCl_4$, determined by the reservoir temperature, was 0.11 cc/pulse. The substrates were cleaned in an ultrasonic bath sequentially using acetone, methanol and de-ionized water for 10 min, and then dried with N_2 gas before introducing into the vacuum chamber. Prior to deposition, the chamber was evacuated to a base pressure of 3×10^{-3} torr. To investigate the oxidation resistance of TiN films, five types of samples with substrate temperatures of 300, 350, 400, 450, and 500 ^{o}C were prepared. After deposition, these samples were annealed at temperatures between 300 ^{o}C and 600 ^{o}C with an interval of 100 ^{o}C in O_2 atmosphere.

The thickness of the TiN films was measured by an Alpha-step profilometer, and the sheet resistance by a four-point probe. The film resistivity was then calculated from film thickness and sheet resistance. The film structure was determined by a RIGAKU D/MAX 3.V X-ray diffraction (XRD). The surface quality was characterized by a scanning electron microscope (SEM) and the root-mean-square (RMS) roughness was measured using an atomic force microscope (AFM) over a scanning area of 5μm×5μm in non-contact mode. The film compositions were analyzed by a Fison Microlab 310D Auger electron spectrometer (AES) with incident electron energy of 10 keV.

RESULTS AND DISCUSSION

Fig. 1 shows the growth rate of TiN films as a function of deposition temperature between 300 ^{o}C and 500 ^{o}C. The growth rate is about 0.03 nm per deposition cycle, and almost not affected by deposition temperature. The constant growth rate indicates that the reactions are overall self-limited by the saturated surface adsorption of reactants. The stable adsorption amount of $TiCl_4$ and NH_3 make them suitable for ALD TiN process. The total film thickness is about 30 nm.

The sheet resistances (Rs) of the as-deposited and annealed TiN films are shown in Fig. 2. Unlike growth rate, the Rs of the as-deposited TiN films strongly depends on the deposition temperature. It decreases from 510 to 66 Ω/□ as the deposition temperature increases from 300 to 500 ^{o}C. After thermal O_2 annealing, the Rs of TiN films increases with increasing annealing temperature. The increase amount, however, relies on the film quality. At annealing temperature of 300 ^{o}C, the Rs is unchanged for TiN films grown at 500 ^{o}C, but 5 and 10% increase for TiN films grown at 400 and 300 ^{o}C. At annealing

temperature of 400°C, the Rs are 34, 47, and 74% increase for TiN films grown at 500, 400, and 300 °C respectively. At annealing temperature of 500 °C, the Rs are 232 and 953% increase for TiN films grown at 500 and 400 °C, whereas the Rs is too high to measure (>150000% increase) for TiN films grown at 300 °C. The different increase amount on Rs indicates the oxidation resistance of TiN films is highly affected by deposition temperature.

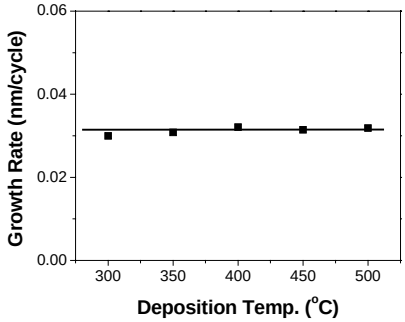

Figure 1. The growth rate of TiN films on SiO_2/Si substrates as a function of deposition temperature.

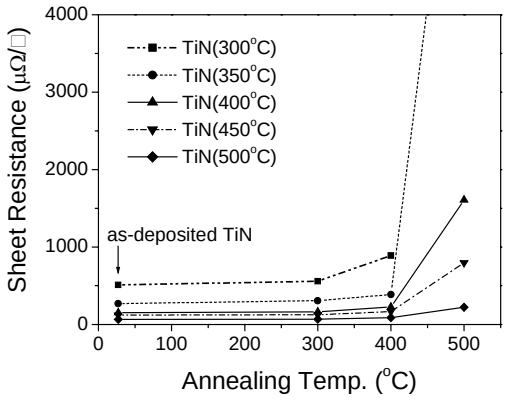

Figure 2. The dependence of sheet resistance on annealing temperature for TiN films grown at indicated deposition temperatures. The annealing was proceeded in O_2 atmosphere for 60 min.

Fig. 3a shows the AES depth profiles of the as-deposited TiN films. The Cl concentration is about 2.5 at.% for TiN films grown at 300°C, whereas below the detection limit (approximately 1 at.%) of AES for films grown above 400 °C. Fig. 3b shows the AES depth profiles of these films after 1 hr annealing in O_2 atmosphere at 500 °C. For films grown at 300 °C, the oxygen is uniformly distributed throughout the film, i.e. the TiN was thoroughly oxidized to form TiO_2. For films grown at 400 °C, about one quarter of the TiN in depth was oxidized. For films grown at 500 °C, however, there is no clear oxidation layer except the higher oxygen concentration in the film as compared with the as-deposited one. The

superior oxidation resistance of TiN films grown at 500 ^{o}C is thought to be due to the lower Cl residues and higher film density, which need further investigation.

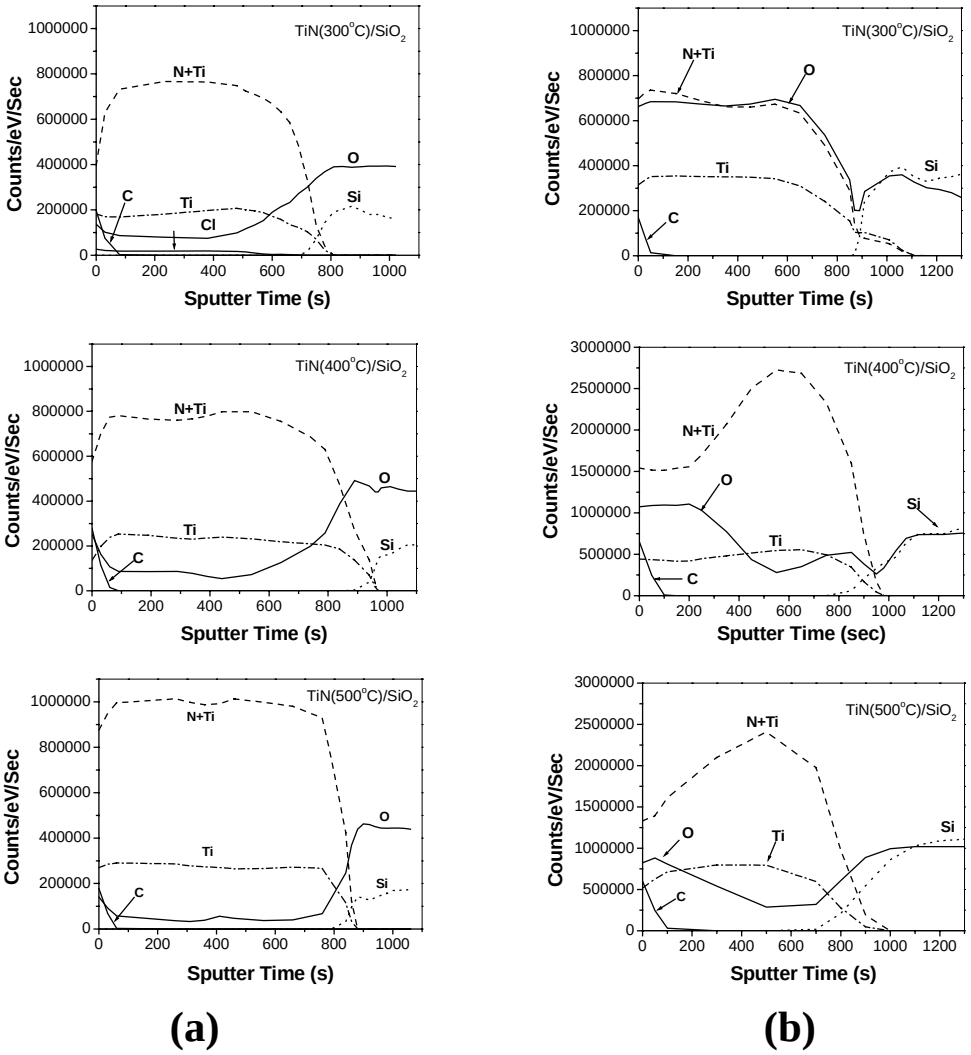

Figure 3. The AES depth profile of TiN/SiO_2 structure with (a) as-deposited TiN films and (b) annealed films. The indicated temperatures are the TiN deposition temperatures. The annealing was proceeded in O_2 atmosphere for 1 hr at 500 ^{o}C.

Fig. 4 shows the XRD patterns of TiN films after 1 hr O_2 annealing at 500 ^{o}C. The XRD patterns are consistent with the AES depth profiles. Only TiO_2 diffraction peaks were found in the films grown at deposition temperature below 350 ^{o}C, but both TiN and TiO_2 peaks were found in the films grown at higher deposition temperature such as 400 ^{o}C. However, no TiO_2 diffraction peaks were found in the films grown at deposition temperature above 450 ^{o}C.

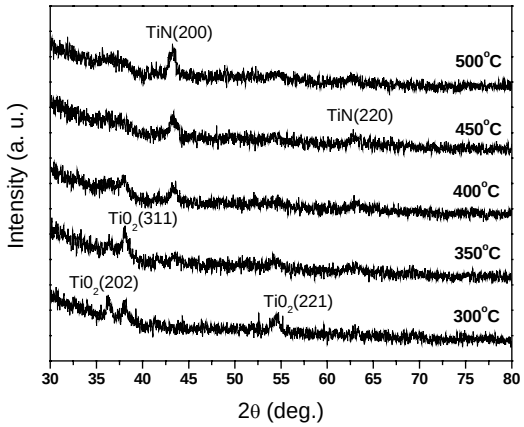

Figure 4. The XRD patterns show the effect of TiN deposition temperature on the film structure after 1 hr O_2 annealing at 500 ^{o}C. The indicated temperatures are the TiN deposition temperatures.

Fig. 5 shows the surface morphologies of various as-deposited and annealed TiN films. The RMS surface roughness values are 2.2, 0.8, and 0.6 nm for films grown at 300, 400, and 500 ^{o}C respectively. After 1 hr O_2 annealing at 500 ^{o}C, the RMS values become 42, 3.5, and 0.6 nm respectively. The surface morphology of TiN films grown at 500 ^{o}C is almost unchanged after 1 hr O_2 thermal annealing at temperature up to 500 ^{o}C, whereas some domes were formed in TiN films grown at 300 ^{o}C due toTiO_2 formation which results in volume expansion.

CONCLUSIONS

ALD TiN films were grown on thermal SiO_2 substrates by means of sequential pulses of $TiCl_4$ and NH_3. The growth rate is about 0.3 nm per deposition cycle and almost independent of the deposition temperature in the range of 300-500^{o}C. The oxidation resistance, however, highly depends on the deposition temperature. The AES depth profiles and XRD patterns show that the films grown at 300 ^{o}C were oxidized to form TiO_2 throughout the film after 1 hr O_2 annealing at 500 ^{o}C; the films grown at 400 ^{o}C were about one quarter of the TiN in depth was oxidized to form TiO_2; whereas no TiO_2 diffraction peaks were found for the films grown at 500 ^{o}C. The surface morphology and film conductivity are still good for the films grown at 500^{o}C after 1 hr O_2 thermal annealing at temperature up to 500 ^{o}C.

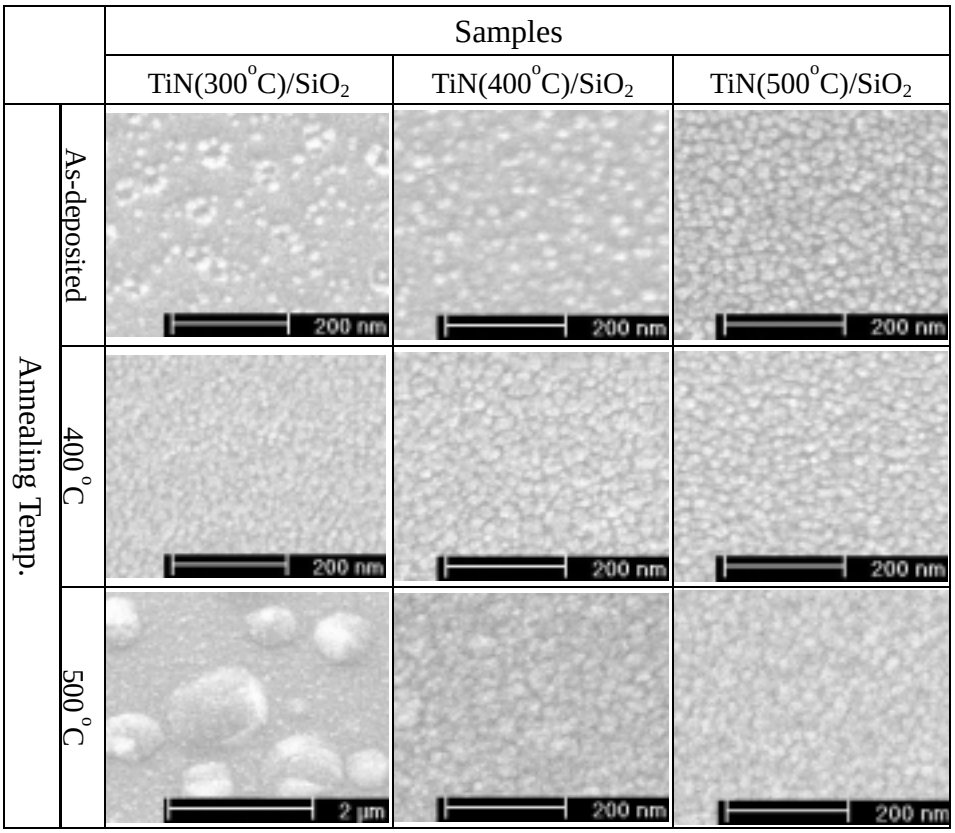

Figure 5. The effect of annealing temperature on the surface morphology of TiN films grown at 300, 400, and 500 °C respectively. The annealing was proceeded in O_2 atmosphere for 1 hr.

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