Material properties and effective work function of reactive sputtered TaN gate electrodes*

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Abstract: The resistivity, crystalline structure and effective work function (EWF) of reactive sputtered TaN has been investigated. As-deposited TaN films have an fcc structure. After post-metal annealing (PMA) at 900 ℃, the TaN films deposited with a N_2 flow rate greater than 6.5 sccm keep their fcc structure, while the films deposited with a N_2 flow rate lower than 6.25 sccm exhibit a microstructure change. The flatband voltages of gate stacks with TaN films as gate electrodes on SiO_2 and HfO_2 are also measured. It is concluded that a dipole is formed at the dielectric-TaN interface and its contribution to the EWF of TaN changes with the Ta/N ratio in TaN, the underneath dielectric layer and the PMA conditions.

Key words: metal gate; thermal stability; effective work function; dipole

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1. Introduction

As complementary metal–oxide–semiconductor (CMOS) devices continue to scale down in size, ultrathin gate dielectrics with an equivalent oxide thickness (EOT) of around 10 Å are needed. At this gate thickness, SiO_2 is too leaky to be employed in low power applications[1]. So high-k materials such as HfO_2, ZrO_2, their silicates and nitrides have been considered to replace SiO_2 with the advantages of a thin EOT, due to high dielectric constants, and small leakage current, due to the adoption of a large physical thickness[2−4]. The conventional poly-Si gate electrode has limitations: poly-Si depletion effects, dopant penetration effects and incompatibility with high-k materials, such as Fermi-level pinning at the HfO_2/poly-Si interface[5, 6]. Refractory metal or metal–nitride gates are then adopted as gate electrodes. The requirements for the metal gate electrodes are as follows: (1) proper work functions, (2) low sheet resistance, (3) high thermal stability, and (4) compatibility with high-k dielectrics and integration technology[7]. Among the proposed advanced gate electrodes, TaN gates are promising candidates because of their thermal stability and compatibility with high-k gate dielectrics[8]. Reactive sputter is a very common way to deposit TaN. Depending on the ratio of Ar and N_2 flow rates, chamber pressure and power density, the atomic ratio of Ta versus N in TaN films can be very different. This will result in different microstructures, thermal stability and other material properties. Kang *et al.*[8] have studied the effects of varying N_2 flow rates (0 to 20 sccm) on the structural properties of sputtered TaN films. They found that with fixed Ar flow rates, power densities and chamber pressures, as-deposited TaN films have a single fcc structure with a ratio of Ta : N $\approx$ 1 : 1 for a N_2 flow rate at 8 and 10 sccm. Valleti *et al.*[9] also investigated the structural properties of TaN films by reactive sputter. Depending on the N_2/Ar ratio, several different phases may exist in the as-deposited TaN films. This indicates that the structural properties of TaN depend critically on the specific chamber structure of a sputter machine and sputter conditions such as the N_2/Ar ratio.

The work function of a gate electrode metal is important for CMOS applications. With the formation of a dipole between the gate oxide and the metal, the effective work function (ϕ_m (EWF)) becomes an important physical quantity in determining the flatband voltage (V_{fb}) of the MOS capacitors[10−12]. It has two components: the vacuum work function of a metal and the interface dipole between the metal and the dielectric underneath. Sugimoto *et al.*[10] observed that the values of ϕ_m (EWF) for as-deposited radio-frequency sputtered TaN on SiO_2 and HfO_2 were 4.44 eV and 4.62 eV, respectively. Both values increased after PMA above 600 ℃. With PMA at 900 ℃, the EWF on SiO_2 and HfO_2 increased to 4.56 eV and 4.77 eV, respectively. After selectively etching away TaN, Ta-oxide is found to remain on the surface of SiO_2 (or HfO_2). The formation of Ta_2O_5 at the interface between SiO_2 (or HfO_2) and TaN is attributed to the origin of the dipole. Both the underneath dielectric materials and the PMA conditions affect the effective work function of TaN films[9, 10]. As a TaN target and Ar-only sputtering gas is used, the Ta/N ratio in TaN films is fixed in their experiments.

The thermal stability of sputtered TaN films has not yet been thoroughly investigated. How does the microstructure of TaN change after PMA? As the phases of TaN critically depend on the N_2/Ar ratio during sputtering, it is very valuable to investigate how the N_2/Ar ratio affects thermal stability and ϕ_m (EWF) of TaN as a gate electrode. The study in this paper is based on Kang's work[8]. Using the same Kurt J Lesker sputter machine, we finely varied the N_2 flow rate in a range so that

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the as-deposited TaN films had a fcc structure. The sheet resistance, crystalline structure and EWF of TaN films on SiO_2 and HfO_2 have been studied as a function of N_2 flow rate and PMA conditions.

2. Experiments

To investigate the material properties of TaN films, 200 nm film was reactively sputtered on thermally grown 350 nm thick SiO_2/Si (100) substrates by direct current magnetron sputtering from a 6 inch Ta target in a Kurt J Lesker sputter machine. No intentional substrate heating was used. By fixing the power density at 6 W/cm^2, the pressure at 10 mTorr pressure and the Ar flow rate at 20 sccm, a N_2 flow rate was varied from 6 to 7.75 sccm with a step of 0.25 sccm. Outside of this range of N_2 flow rate, TaN films are found either too nitrogen deficient or too nitrogen rich. After deposition, samples were divided into two splits. One split went through a PMA of 900 ℃/1 min in N_2 to examine thermal stability; the other split skipped this step. Sheet resistance was measured by the four-probe method. Crystalline structures were measured using glancing angle X-ray diffraction (XRD) with a Cu Kα source.

TaN-gated MOS capacitors were also fabricated. Two studied gate stacks were S1 of TaN/4 nm SiO_2/p-Si and S2 of TaN/5 nm HfO_2/4 nm SiO_2/p-Si. 4 nm SiO_2 was thermally grown at 850 ℃ in dry O_2. 5 nm HfO_2 was deposited by sputtering from a Hf target with a post-deposition annealing (PDA) of 500 ℃/5 min in N_2. After forming gate dielectrics on 4 inch Si (100) wafers, for each gate stack, 200 nm TaN film was deposited with eight different N_2 flow rates. After patterning the TaN, each sample was further divided into 2 pieces and one of the two pieces went through a PMA of 900 ℃/1 min in N_2. Finally, an Al backside contact was deposited and annealed in forming gas at 400 ℃ for 30 min.

3. Results and discussion

TaN thickness was measured as follows. First, TaN film was sputtered for 5 min on a photoresist patterned Si wafer and then TaN square patterns were formed using a lift-off process. A step profiler was used to measure the TaN thickness. It was found that varying the N_2 flow rate in the range used in this study did not affect TaN deposition rate very much. Figure 1 shows the dependence of TaN resistivity on the N_2 flow rate without and with PMA at 900 ℃/1 min in N_2. The resistivity was calculated from the measured sheet resistance (R_s) × TaN thickness (t). With increasing the N_2 flow rate from 6 to 7.75 sccm, the resistivity of as-deposited TaN films increased from 258 to 744 $\mu\Omega$·cm. In contrast, the resistivity of TaN film after PMA was 93 $\mu\Omega$·cm for 6 sccm N_2 and 101 $\mu\Omega$·cm for 6.25 sccm N_2. For N_2 with a flow rate $\geqslant$ 6.5 sccm, the resistivity of annealed TaN films increased from 402 $\mu\Omega$·cm for 6.5 sccm N_2 to 1081 $\mu\Omega$·cm for 7.75 sccm N_2.

In order to examine how the microstructure changed after PMA, a glancing angle XRD was performed. Figure 2 shows XRD spectra without (thick solid) and with (thin solid) PMA for N_2 flow rates ranging from 6.0 to 7.75 sccm. All as-deposited TaN films has fcc-cubic structures with clear (111) and (200) peaks. The intensity of (220) peak decreased with increasing N_2 flow rate. After PMA, for depositing N_2 flow rate $\geqslant$ 6.5 sccm, the fcc phase still exists, but with some position shifts for all peaks, indicative of a strain change. For depositing N_2 flow rates at 6.0 and 6.25 sccm, the data showed that there was a more complicated structural change in the TaN films. Figure 3 shows a comparison of XRD spectra at these two N_2 flow rates with data from Ref. [9]. Peaks are tentatively identified as $TaN_{0.8}$ (hexagonal), TaN (fcc-cubic) and Ta_4N (orthogonal). Apart for fcc-cubic TaN, the other two phases are Ta-rich, indicating that some N atoms escaped after PMA in the TaN films with a depositing N_2 flow rate at 6.0 and 6.25 sccm.

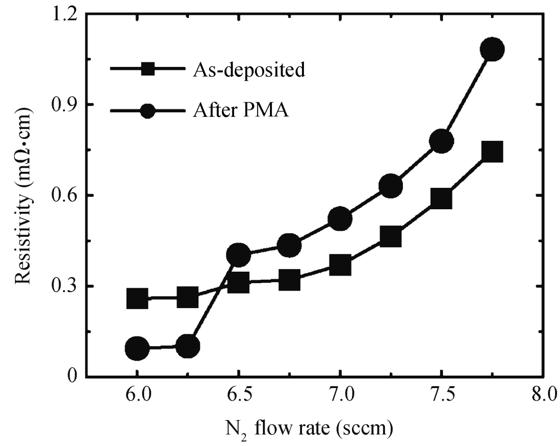

Fig. 1. Resistivity of 200 nm TaN films versus N_2 flow rate: as-deposited and after a PMA of 900 ℃/1 min in N_2.

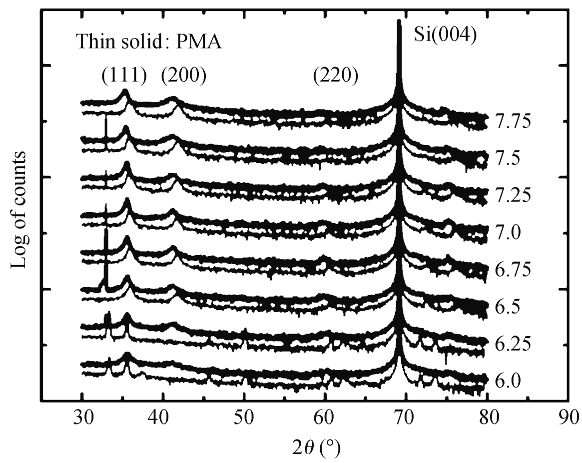

Fig. 2. Glancing angle XRD spectra of TaN films versus depositing N_2 flow rate: as-deposited (thick solid) and after a PMA of 900 ℃/1 min in N_2 (thin solid).

Two kinds of TaN-gated MOS capacitors were fabricated with gate stacks of S1: TaN/4 nm SiO_2/p-Si and S2: TaN/5 nm HfO_2/4 nm SiO_2/p-Si. The capacitor area was 1.22 × 10^{-4} cm^2. High frequency (HF) capacitance–voltage (CV) curves were measured at 1 MHz and were simulated using the popular CVC program[13]. Figure 4 shows the measured HF, simulated HF and LF (low frequency) CV curves for a capacitor with gate stack S1 and PDA-only. The N_2 flow rate was 7.25 sccm. It can be seen that the measured and simulated HF CV curves agree with each other excellently. The extracted V_{fb} and EOT

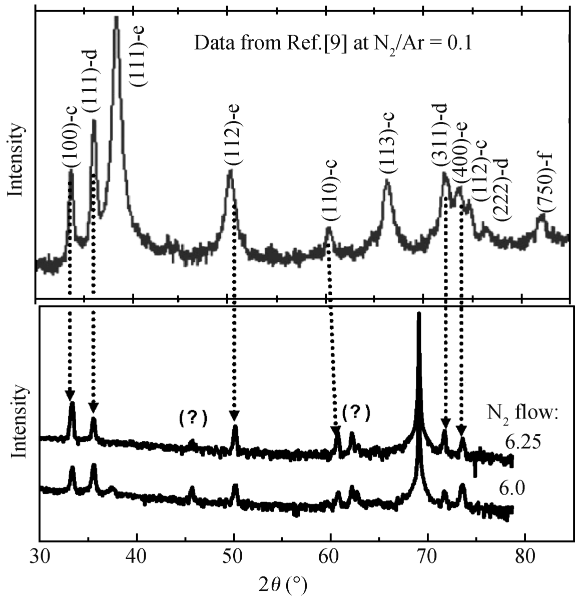

Fig. 3. Comparison of XRD spectra of TaN films (N_2 flow rate: 6.0 and 6.25 sccm) after PMA with the data of Ref. [10]. The four phases in the data of Ref. [10] are: c-$TaN_{0.8}$ (hexagonal), d-TaN (fcc cubic), e-Ta_4N (orthogonal) and f-$TaN_{0.04}$ (cubic).

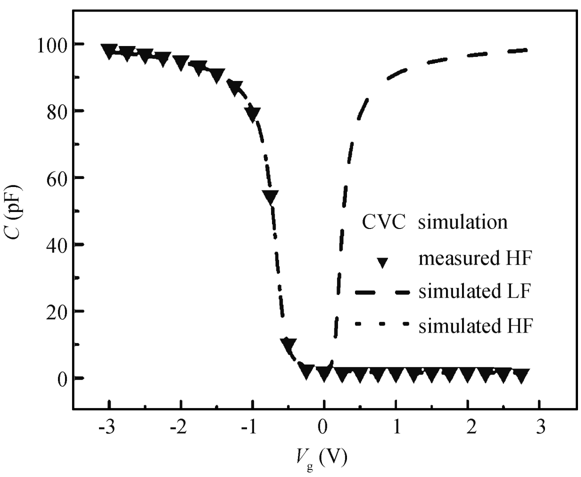

Fig. 4. Measured HF, simulated HF and LF CV curves for a capacitor with gate stack S1 and PDA-only using CVC program. The N_2 flow rate was 7.25 sccm. The extracted V_{fb} and EOT are –0.554 V and 3.91 nm, respectively.

are –0.554 V and 3.91 nm, respectively. Similar parameters are also extracted for other capacitors. V_{fb} values of MOS capacitors with gate stacks of S1 and S2 without and with PMA are shown in Fig. 5(a). Theoretically, V_{fb} in S1 can be written as[13]

$$qV_{fb} = [\phi_m(\text{EWF}) - \phi_s] - Q_f t_{ox}/\varepsilon_{SiO_2}, \\ = [\phi_m(\text{Vac}) + \Delta_d - \phi_s] - Q_f t_{ox}/\varepsilon_{SiO_2}. \quad (1)$$

Here q, ϕ_m(Vac), ϕ_s, Q_f, t_{ox}, and ε_{SiO_2} are electron charge, vacuum work functions of gate electrode, the Fermi level of the Si substrate, oxide fixed charge density, SiO_2 thickness and dielectric constant of SiO_2, respectively. Δ_d is the contribution to V_{fb} from the dipole at the SiO_2/TaN interface and ϕ_m (EWF)

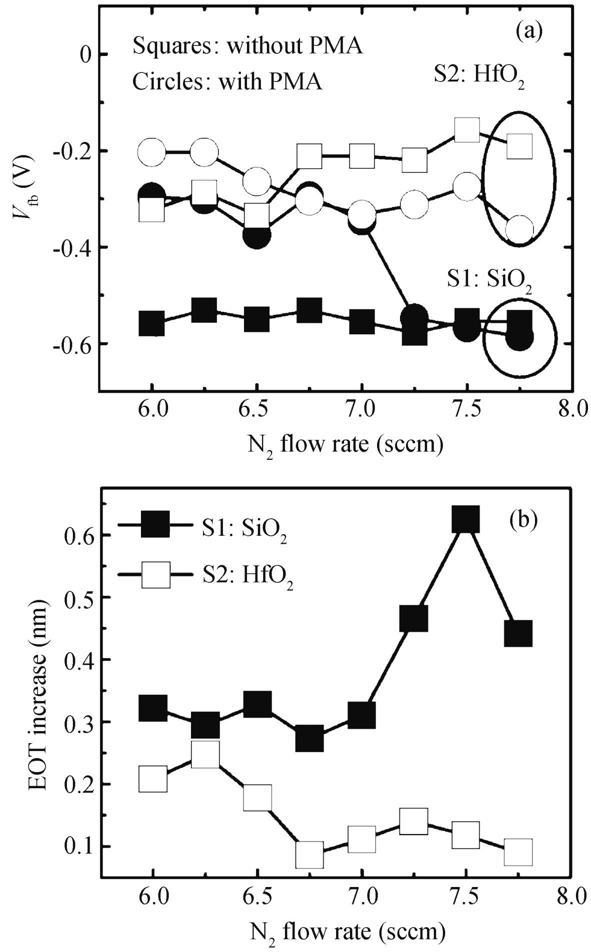

Fig. 5. TaN-gated MOS capacitors with gate stacks of S1: TaN/4 nm SiO_2/p-Si (called as SiO_2) and S2: TaN/5 nm HfO_2/4 nm SiO_2/p-Si (called as HfO_2). (a) V_{fb} versus N_2 flow rate for cases of without and with a PMA of 900 ℃/1min in N_2. (b) EOT increase versus N_2 flow rate after the PMA.

is the effective work function of TaN on SiO_2. With varying SiO_2 thickness, the y intersection and the slope correspond to $\phi_m(\text{EWF}) - \phi_s$ and Q_f, respectively. In present paper, only one thickness (4 nm) of SiO_2 was grown, so the term of $Q_f t_{ox}/\varepsilon_{SiO_2}$ is the same for all capacitors in S1. Ignoring this term, an approximate value of ϕ_m(EWF) can be determined from V_{fb}. The value of ϕ_s is 4.9 eV for the p-type substrate (N_A: 2 $\times 10^{15}$ cm^{-3}). For S2, similar equations can be written. It should be noted that here Δ_d is the contribution to V_{fb} from the dipole at the HfO_2/TaN interface and ϕ_m(EWF) is the effective work function of TaN on HfO_2. From Fig. 4(a), V_{fb} values of as-deposited TaN films on SiO_2 (S1) were about –0.55 V for all N_2 flow rates; while V_{fb} values of as-deposited TaN films on HfO_2 (S2) were higher, increasing from –0.32 V (6.0 sccm) to –0.19 V (7.75 sccm). With PMA, V_{fb} values of TaN films on SiO_2 (S1) were about –0.3 V for N_2 flow rates ranging from 6.0 to 7.0 sccm, and still about –0.55 V for N_2 flow rates ranging from 7.25 to 7.75 sccm. For TaN films on HfO_2 (S2), the V_{fb} values of annealed samples decreased from –0.2 V (6.0 sccm) to –0.367 V (7.75 sccm) with an increasing N_2 flow rate. From our approximation of $\phi_m(\text{EWF}) \cong V_{fb} + \phi_s$ and $\phi_s = 4.9$ eV, ϕ_m(EWF) of as-deposited TaN films on SiO_2 was about 4.35

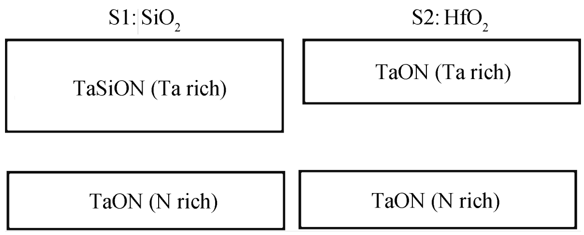

Fig. 6. Schematic diagrams of interfacial layer formation after a PMA of 900 ℃/1 min in N_2 for S1 and S2 under Ta-rich and N-rich conditions.

eV for all N_2 flow rates. After PMA, it increased to 4.6 eV for 6.0 to 7.0 sccm N_2, and still about 4.35 eV for 7.25 to 7.75 sccm N_2. ϕ_m(EWF) for as-deposited TaN films on HfO_2 increased from 4.58 eV (6.0 sccm) to 4.71 eV (7.75 sccm). After PMA, it decreased from 4.7 eV (6.0 sccm) to 4.53 eV (7.75 sccm).

Figure 5(b) shows the EOT increase of gate stacks after PMA. In S2, the EOT increase was larger for low N_2 flow rates after PMA. The reason is that Ta-rich TaN films are easier to oxidize than N-rich TaN films. In contrast, in S1, the EOT increase was less for low N_2 flow rates due to the mixing of SiO_2 and Ta-rich TaON and the formation of high-k TaSiON at the SiO_2/TaN interface; for high N_2 flow rates, due to less oxidation of N-rich TaN films, the higher EOT increase should be due to more SiO_2 growth at SiO_2/Si interface. Figure 6 schematically shows the formation of the different interfacial layers at the SiO_2/TaN and HfO_2/TaN interfaces. The property change of these interfacial layers gives rise to a variation of the dipole contribution Δ_d to V_{fb}. From the data of resistivity, surface morphology and XRD, it is expected that the vacuum work function of TaN films should also depend on Ta/N ratio and PMA conditions.

4. Conclusions

In summary, the resistivity, crystalline structure and effective work function of sputtered TaN films are shown to vary as a function of N_2 flow rate, the underneath dielectric layer and post-metal annealing conditions. Forming different interfacial layers at the interface between the dielectric layer (SiO_2 or HfO_2) and TaN gives rise to a varying dipole contribution to the flatband voltage and the effective work function.

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