Growth mechanism of TiN film on dielectric films and the effects on the work function

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Available online 11 February 2005

Abstract

We have investigated the growth mechanism of ALD-TiN film on different dielectrics and the resulting effective work function value. TiN nucleation rate and growth rate are found to be dependent on the dielectric films. TiN growth mechanism changed from 3-D type on SiO\textsubscript{2} to layer-by-layer type on HfO\textsubscript{2}. The minimum TiN thickness required for a complete surface coverage varies according to the growth mechanism. Capacitor (MOSCAP) characterization revealed that the effective work function of TiN is dependent not only on dielectric films but also on the TiN thickness. The behavior of work function and fixed charge correlated with the growth mechanism of TiN on dielectric films.

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Keywords: MOSFET; Metal gate electrode; High-\textit{k} gate dielectric; TiN; Atomic layer deposition; Work function

1. Introduction

Metal gate processes have been investigated in order to address the limitations of poly silicon gate electrodes such as poly depletion, high resistance, boron penetration and compatibility issues with high-\textit{k} gate dielectric films in sub-50 nm CMOS technology nodes \cite{1}. Metal work function is the key material property for gate electrode applications, but it is generally difficult to obtain the desired work function value of a metal when it is deposited on high-\textit{k} dielectric films \cite{2}. Metal induced gap state (MIGS) theory partially explains the pinning mechanism with dipole generation at the metal/dielectric interface \cite{3}, but extrinsic causes such as chemical reactions and inter-diffusion of atoms at the metal/dielectric interface should be taken into account to describe the pinning phenomena \cite{4}. The work function is known to depend on the crystallographic orientation also \cite{5}. To address these questions, a study on the initial growth mechanism is very important since the first couple of metal layers determine the physical/chemical nature of the interface and likely to play an important role in effective work function. Atomic layer deposition (ALD) of metal film is appropriate for this approach because of the atomic level control of the film thickness. Furthermore, ALD is a preferred deposition for the future process for metal gates because of its low impurity levels, conformal deposition and no damage to the underlying dielectric layer \cite{6,7}. In this work, we report the evolution of the microstructure and work function value of TiN as a function of thickness on different dielectric layers by using ALD-TiN process.

2. Experimental

For physical analysis, 100 Å thick HfSiO\textsubscript{x} (20% Si) and HfO\textsubscript{2} layers were grown by ALD process on silicon
wafers. These films were annealed at 700 °C in NH₃ ambient for 1 min. A 100 Å thick SiO₂ film was grown by thermal oxidation of bare silicon wafer. TiN deposition was carried out on each dielectric film with 5–100 cycles by TiN-ALD process based on TiCl₄+NH₃ chemistry at 550 °C. Total reflection X-ray Fluorescence (TXRF), X-ray Diffraction (XRD), X-ray Reflectometry (XRR), Atomic Force Microscopy (AFM) and scanning electron microscope (SEM) measurements were conducted for physical analysis of TiN films.

Highly doped p-type 8 in. Si (100) wafers were used for MOS-capacitor fabrication. MOS capacitors with TiN gate electrode deposited on SiO₂, HfSiOₓ and HfO₂ gate dielectrics were fabricated on terraced oxide structure that has four different oxide thicknesses on one wafer [8]. Starting with 100 Å thermally grown oxide, terraced oxide structure has been etched into steps with 20/40/60/80 Å of thicknesses. A 30 Å HfSiOₓ film (20% SiO₂) and a 30 Å HfO₂ film were deposited by ALD on terraced oxide. HfSiOₓ and HfO₂ films were subject to post deposition anneal at 700 °C in NH₃ ambient. Varied thickness of TiN film (0–100 cycles) was deposited by ALD method on top of terraced oxide directly or on high-k layers. The deposition rate of TiN film was ~1.2 Å with this process condition. After TiN deposition, 1.5 kÅ n⁺poly-silicon was deposited. For dopant activation, gate stack underwent 1000 °C, 30 s rapid thermal annealing. For probing purposes, the poly silicon was silicided with cobalt and Al film was deposited on the backside of the wafer.

### 3. Results and discussion

In order to investigate the nucleation of TiN islands on the dielectric films, the microstructure of the surface was observed by SEM. Fig. 1 shows the morphology evolution of TiN growth. At 5 cycles, the island density of TiN grains is the lowest on SiO₂ surface compared to the other dielectric surfaces. This trend is reflected in the final grain sizes of 100 cycle samples and a larger and fewer numbers of grains are found on SiO₂ surface. The difference of TiN film morphology between HfO₂ and HfSiOₓ surface is not clear due to the limited resolution of SEM pictures.

Fig. 2a shows the Ti signal obtained from TXRF measurement as a function of TiN deposition cycle. TiN growth rate on HfO₂ surface is relatively close to a constant. On the other hand, the TiN growth rate on SiO₂ surface shows distinct slope change around 20 cycles of TiN deposition. The presence of inflection point is indication that a major change in growth mode occurs in the proximity of this point and it is most likely to be a complete coverage of the dielectric surface with TiN. Based on this assumption, the time required for a complete coverage with TiN is longest on SiO₂ surface while the growth rate of TiN on HfSiOₓ is intermediate. The reflection angle at which the Ti peak detected is plotted in Fig. 2b. Since the low reflection angle implies low density or rough surface, data shown in Fig. 2a and b strongly suggest that the initial TiN growth mechanism is more three-dimensional on SiO₂ surface while more two-dimensional growth on HfO₂ surface. Assuming identical
sticking coefficient of TiN atoms on residing TiN film, the slower increase of the density of the TiN film on SiO₂ surface can be accounted as due to higher roughness. The surface microroughness values shown in Table 1 correlate very well with the data in Fig. 2. It is clear that the initial roughness of the dielectric surface has little effect on that generated by the TiN deposition. The increase of peak-to-valley roughness with the deposition of TiN, which is indicative of the vertical dimension of the film morphology is in the order that is expected in the result of Fig. 1b.

We propose that a catalytic effect of Hf atoms on HfSiOₓ and HfO₂ surface may facilitate an easier dissociation of ALD precursors and thus enhance the nucleation of TiN film. Catalytic effect of transient metals in chemical reactions has been suggested previously [9]. The minimum layer thickness required for complete surface coverage is valuable information in determining work function of a metal without considering the interference from capping layer such as poly silicon. In our work, the minimum layer thickness for a complete layer formation is estimated as ∼24 Å for SiO₂, ∼12 Å for HfSiOₓ and ∼6 Å for HfO₂ by X-ray reflectivity study respectively [10] (not shown). We compared the XRD spectrum of as-deposited 100 Å TiN films. The only phase detected is fcc TiN regardless of dielectrics and there is no predominantly preferred orientation. This indicates that the dielectric surface has negligible effect on the crystallographic properties of grown TiN film.

Capacitance–voltage (C–V) measurement (at 100 kHz) was carried out and $V_{fb}$ and capacitor equivalent thickness (CET) values are determined by fitting the measured high frequency (at 100 kHz) curves with theoretical ones. Flatband voltage values from each TiN/dielectric stack are plotted against CET and the effective work function values were extracted from the $V_{fb}$ intercept. It is noteworthy that reliable linear regressions in $V_{fb}$–CET plots have been obtained from all samples by using terraced oxide structure. Fig. 3 shows the effective work function values against TiN deposition cycle. Data from n+poly electrode were added as a reference. Effective work function of TiN films in our experiment is in the range of 4.2–4.6, which is a slightly lower value than reported but the process dependence should be taken into account [11,12].

In addition to the shift of work function values at higher energy level than that of TiN/SiO₂ stack, it is found that the

<table>
<thead>
<tr>
<th>SiO₂</th>
<th>HfSiOₓ</th>
<th>HfO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_{rms}$ (Å)</td>
<td>$R_{max}$ (Å)</td>
<td>$R_{rms}$ (Å)</td>
</tr>
<tr>
<td>No TiN</td>
<td>1.2</td>
<td>11.2</td>
</tr>
<tr>
<td>5 cycle TiN</td>
<td>5.7</td>
<td>39.1</td>
</tr>
<tr>
<td>10 cycle TiN</td>
<td>4.5</td>
<td>40.1</td>
</tr>
<tr>
<td>20 cycle TiN</td>
<td>4.0</td>
<td>41.0</td>
</tr>
</tbody>
</table>
The effective work function of the TiN gate is a function of TiN thickness. The change of TiN work function may suggest that the penetration of the tail of electron wave function of n+poly through very thin TiN layer occurs. However, possible effects from extrinsic causes such as interfacial reaction or stoichiometry change with film thickness due to diffusion may not be ruled out [11]. In TiN/SiO₂ samples, \( V_{fb} \) is not changed until 10 cycles while \( V_{fb} \) increases continuously from 5 cycles in TiN/HfSiO\(_x\), which is consistent with the observations in TiN growth study. Considering the 0.2 eV difference between n+poly data, it is clear that the effective work function abruptly changes as soon as TiN atoms deposited on dielectric surface even before the coverage of the surface is completed. The effective work function of TiN/HfO₂ stack is lower than TiN/HfSiO\(_x\) and the increase is less linear than expected. This deviation from the prediction of MIGS theory based on dipole creation [2] can be attributed to the chemical reaction at this particular metal/dielectric interface. Note that the capacitor samples underwent 30 s anneal at 1000 °C. Further study is ongoing on this subject.

Fixed oxide charge densities of gate stacks calculated from the slope of the linear regression of the \( V_{fb} \)–CET curves are plotted in Fig. 4. It is found that the fixed charge also slightly increases with TiN thickness. The elongated process time for thicker TiN deposition appears to be the cause of this increase. The highest charge density of TiN/ HfO₂ stack accounts for the high bulk charges in HfO₂. When the n+poly gate is replaced with TiN, fixed charge of the gate stack changes even with dielectric layer is the same, more significantly on SiO₂. With TiN, the difference between dielectrics is negligible. This implies that the charge state of the bonding at the metal/dielectric interface plays an important role in determining effective work function and fixed charge of a gate stack.

4. Conclusions

We have investigated the growth mechanism of ALD-TiN film on different high-\( k \) dielectrics. TiN grows in more two-dimensional manner from the HfO₂ compared to the mechanism on SiO₂. This resulted in highest TiN thickness for the complete coverage for SiO₂ and lowest thickness in case of HfO₂. Hf atoms at the interface are proposed to facilitate fast and uniform nucleation of TiN film. The correlation between growth mechanism and the microstructure of TiN film was not observed and so was work function. It has been found that the effective work function of TiN is a function of TiN thickness as well as underlying dielectric. Fixed oxide charge data indicates that the charge state of the chemical bonding at the metal/dielectric interface is an important factor in determining work functions and fixed charge density of gate stack.

References