Interface formation and thermal stability of advanced metal gate and ultrathin gate dielectric layers

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The compatibility of metallic titanium nitride (TiN_x) films for advanced gate electrodes and remote plasma enhanced chemical vapor deposited silicon oxide (SiO_2) or silicon oxide/silicon nitride (Si_3N_4) advanced gate dielectric layers is investigated by interrupted growth and on-line rapid thermal annealing using on-line Auger electron spectroscopy. Growth of TiN_x on SiO_2 and Si_3N_4 occurs uniformly without a titanium seed layer. $\text{TiN}_x/\text{SiO}_2$ and $\text{TiN}_x/\text{Si}_3\text{N}_4$ interfaces are chemically stable against reaction for rapid thermal annealing treatments below 850 °C. Metal-oxide-semiconductor capacitors using TiN_x gate contacts and SiO_2 or $\text{SiO}_2/\text{Si}_3\text{N}_4$ gate dielectrics exhibit excellent $C-V$ characteristics. The measured $\text{TiN}_x/\text{SiO}_2$ barrier height in these devices is $\Phi_b = 3.7 \pm 0.1$ eV. The observed difference in fixed charge for SiO_2 and $\text{SiO}_2/\text{Si}_3\text{N}_4$ dielectrics is briefly discussed in terms of a new interface dipole model. © 1998 American Vacuum Society. [S0734-211X(98)11704-3]

I. INTRODUCTION

The continuing effort to reduce metal-oxide-semiconductor (MOS) device dimensions has led to considerable interest in silicon oxide¹ (SiO_2) and silicon oxide/silicon nitride^{2,3} (Si_3N_4) layered films with an equivalent oxide thickness $t_{\text{ox-eq}} < 3$ nm for advanced gate dielectrics. Similarly, to maintain proper device scaling and to avoid the effects of gate electrode depletion, attention is being focused on advanced gate materials such as metallic titanium nitride⁴⁻⁸ (TiN_x) as a possible replacement for heavily doped polycrystalline silicon. However, before such materials can be incorporated into device production they must be shown to be compatible with the other materials and with subsequent process conditions required for fabrication. Of particular concern is the possibility of chemical reaction at the interface between these advanced dielectric and gate materials at elevated temperatures.^{9,10} For example, the gate metal/dielectric interface must be able to withstand rapid thermal annealing (RTA) temperatures of at least 800–1000 °C which are required to activate dopants in source and drain structures.

In this article, the interface formation between reactively sputtered TiN_x metallic films and SiO_2 or $\text{SiO}_2/\text{Si}_3\text{N}_4$ dielectric layers prepared by low-temperature remote plasma enhanced chemical vapor deposition (RPECVD) is investigated as well as the chemical stability of these interfaces following on-line RTA treatments up to 850 °C. The evolution of the $\text{TiN}_x/\text{SiO}_2$ and $\text{TiN}_x/\text{Si}_3\text{N}_4$ interfaces is investigated from their initial formation at the monolayer level to the buried interface by interrupted film growth using on-line Auger electron spectroscopy (AES). The stability of $\text{TiN}_x/\text{SiO}_2$ and $\text{TiN}_x/\text{Si}_3\text{N}_4$ interfaces against reaction during RTA treatments at temperatures below 850 °C is also established by on-line AES. Finally, capacitance-voltage ($C-V$) characteristics of MOS capacitors employing TiN_x gate electrodes

with ultrathin single layer SiO_2 and dual layer $\text{SiO}_2/\text{Si}_3\text{N}_4$ gate dielectrics are presented. These $C-V$ results are compared with similar MOS devices made using Al gate contacts.

II. EXPERIMENT

Interrupted growth and chemical stability experiments were conducted on 3 in. *p*-type Si(100) wafers on which either a single layer SiO_2 dielectric or a dual layer $\text{SiO}_2/\text{Si}_3\text{N}_4$ dielectric stack was deposited. In both cases, the SiO_2 layer was 5 nm thick and was prepared by a two-step plasma assisted oxidation/RPECVD process¹ which is described in detail elsewhere. The Si_3N_4 layer was 3 nm thick and was deposited by RPECVD with NH_3 and SiH_4 source gases injected downstream^{2,11,12} at a ratio of 10:1. Prior to TiN_x deposition, the SiO_2 and $\text{SiO}_2/\text{Si}_3\text{N}_4$ dielectric layers were subjected to a 30 s RTA treatment at 900 °C to improve their electrical properties by reducing bond defects.^{13,14} This bonding rearrangement was verified by Fourier transform infrared (FTIR) spectroscopy.

Metallic TiN_x films were deposited at room temperature by reactive dc magnetron sputtering of a 99.9% Ti target at 50 W with a 5:1 mixture of 99.999% Ar and 99.999% N_2 at a chamber pressure of 6 mTorr. Several ultrathin TiN_x layers were deposited sequentially and AES spectra collected until the $\text{Si}_{L_{VV}}$ Auger peak could no longer be observed, indicating that the interface had been buried. Thicker TiN_x layers (each about 0.5–1.0 nm) were then added until bulk characteristics were observed. To study the chemical stability of the metal/dielectric interfaces, a 0.6–1.0 nm thick TiN_x layer was deposited on SiO_2 or $\text{SiO}_2/\text{Si}_3\text{N}_4$ and annealed in vacuum for 180 s in 100 °C steps from 350 to 850 °C. Following each on-line RTA treatment, AES spectra were collected.

MOS capacitors were prepared on *n*-type Si(100) wafers with ultrathin SiO_2 or $\text{SiO}_2/\text{Si}_3\text{N}_4$ dielectrics and TiN_x or Al gate electrodes. The wafers were cleaned, a thermal field

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FIG. 1. FTIR spectra of RPECVD Si_3N_4 dielectric as deposited and following a 30 s 900 °C RTA treatment. The decrease of SiN–H stretch and bending modes while the Si–N asymmetric stretch increases after annealing indicates conversion of SiN–H dangling bonds to Si–N network bonds.

oxide was grown and patterned, and the active area wet chemically etched. The wafers were cleaned again prior to RPECVD deposition of a 3.5 nm SiO_2 gate dielectric or a 2.0 nm SiO_2 /2.0 nm Si_3N_4 dielectric bilayer. The wafers were patterned for liftoff and a 50 nm TiN_x or 100 nm Al gate electrode deposited by sputtering. A 100 nm thick Al layer was sputtered on top of the TiN_x gate to facilitate external contact. Liftoff was performed, Al back contacts evaporated, and the samples were annealed at 300 °C in H_2 for 1800 s. Standard high frequency (100 kHz) C – V measurements were conducted to determine the device characteristics.

III. RESULTS AND DISCUSSION

To evaluate the integration of TiN_x and RPECVD dielectrics with existing Si technology and process flows it is critical to use optimal preparation conditions for these new materials. It has been shown¹³ previously that a 15 s, 900 °C RTA treatment improves the dielectric quality of RPECVD SiO_2 films by reducing the amount of suboxide (SiO_x with $x < 2$) at the Si/ SiO_2 interface and hence the number of electrically active dangling bond defects. A similar improvement in the dielectric reliability of RPECVD Si_3N_4 films occurs¹⁴ by annealing at 900 °C for 30 s and can be monitored with FTIR as seen in Fig. 1. The spectrum displays three main features: a Si–N asymmetric stretching mode at approximately 850 cm^{-1} , a SiN–H bending mode at 1200 cm^{-1} , and a SiN–H stretching mode near 330 cm^{-1} . Figure 1 shows a decrease in the intensity of SiN–H bending and stretching modes while the Si–N asymmetric stretch increases from as-deposited levels following a 900 °C RTA treatment. These changes in the IR spectra have recently been explained¹⁴ as resulting from a conversion of correlated Si–H and SiN–H dangling bonds into Si–N network bonds.

SiO_2 and $\text{SiO}_2/\text{Si}_3\text{N}_4$ dielectric films optimized in this fashion were used to study the interface formation, growth,

FIG. 2. Interrupted growth of TiN_x on RPECVD SiO_2 measured by AES. Si_{LVV} and O_{KVV} peaks decrease while $\text{Ti}_{LVV} + \text{N}_{KVV}$ and Ti_{LMV} peaks increase with additional TiN_x deposition. The asymmetry of $\text{Ti}_{LVV} + \text{N}_{KVV}$ and Ti_{LMV} intensities indicates no Ti seed layer is required.

and chemical stability of TiN_x . Derivative AES spectra demonstrating the growth of TiN_x on RPECVD SiO_2 are provided in Fig. 2 with the relevant Auger transitions indicated. The bottom curve shows the spectrum for the bare SiO_2 dielectric layer. The vertical offset of subsequent curves corresponds to the integrated TiN_x sputtering time elapsed, indicated by the right-hand axis. Film thickness was estimated from the bulk deposition rate of 1.0 nm/min which was determined by cross-sectional scanning electron microscopy on thick samples.

A quantitative difficulty which arises in the TiN_x system is that the Ti_{LVV} and N_{KVV} AES peaks overlap^{15–17} at 385 eV; however the Ti_{LMV} feature at 420 eV does not suffer from this deficiency. For TiN_x , the $\text{Ti}_{LVV} + \text{N}_{KVV}$ and Ti_{LMV} features exhibit a peak to peak intensity ratio that is about 2:1. In contrast, for pure Ti the intensity of these two peaks would be nearly equal.⁸ In Fig. 2 the $\text{Ti}_{LVV} + \text{N}_{KVV}$ feature is seen to form and grow on SiO_2 as additional layers of TiN_x are added and the intensity of this peak is always about twice that of Ti_{LMV} . This asymmetry in these peak intensities, which occurs even for submonolayer coverage, indicates that TiN_x grows directly on SiO_2 without the need for an intermediate Ti seed layer. The Si_{LVV} peak intensity at 76 eV decreases as successive TiN_x layers are deposited and disappears entirely for a metal thickness greater than about 0.8 nm. The O_{KVV} peak near 510 eV also initially decreases; however a small amount of parasitic oxygen is always observed even after the $\text{TiN}_x/\text{SiO}_2$ interface is completely buried and bulk TiN_x features are observed.

Figure 3 shows similar derivative AES spectra for interrupted TiN_x growth on Si_3N_4 . Because the dielectric contains nitrogen, the initial development of the $\text{Ti}_{LVV} + \text{N}_{KVV}$ feature is impossible to observe. However, the Ti_{LMV} peak evolution

FIG. 3. Interrupted growth of TiN_x on RPECVD Si_3N_4 measured by AES. The Si_{LVV} peak decreases while the $\text{Ti}_{\text{LVV}} + \text{N}_{\text{KVV}}$ and Ti_{LMV} peaks increase with additional TiN_x deposition. The similarity in growth of the Ti_{LMV} peak to Fig. 2 suggests that no seed layer is required.

on Si_3N_4 is similar to the behavior observed in Fig. 2 on SiO_2 and suggests that TiN_x grows directly on Si_3N_4 without a buffer layer. The Si_{LVV} peak intensity in Fig. 3 is diminished by successive TiN_x layers and disappears above about 0.8 nm as expected.

The decrease of the Si_{LVV} peak intensity normalized to its value in the bare dielectric is plotted on a log scale as a function of TiN_x deposition time in Fig. 4 for both the SiO_2 and the $\text{SiO}_2/\text{Si}_3\text{N}_4$ substrates. In both cases the intensity decreases exponentially with TiN_x thickness although the slopes differ by about a factor of 2. This exponential de-

FIG. 4. Decrease of normalized Si_{LVV} AES peak intensity with increasing TiN_x deposition on SiO_2 and Si_3N_4 dielectric layers. The exponential decay indicates uniform TiN_x layer growth on both dielectrics.

FIG. 5. Chemical stability of $\text{TiN}_x/\text{SiO}_2$ interface following the RTA treatments indicated. The dramatic increase of the Si_{LVV} AES peak at 850 °C indicates that a reaction has occurred.

crease of the Si_{LVV} peak intensity with TiN_x thickness indicates uniform layer growth on both SiO_2 and Si_3N_4 . The difference in the slopes of these curves corresponds to different deposition rates due to target aging. Detailed kinetics of the interface formation and morphology of the TiN_x layer in each case require further investigation.

Derivative AES spectra for $\text{TiN}_x/\text{SiO}_2$ and $\text{TiN}_x/\text{Si}_3\text{N}_4$ interfaces subjected to on-line RTA treatments up to 850 °C are shown in Figs. 5 and 6, respectively. In both cases, a

FIG. 6. Chemical stability of $\text{TiN}_x/\text{Si}_3\text{N}_4$ interface following the RTA treatments indicated. A slight increase of the Si_{LVV} AES peak at 850 °C indicates that the interface is chemically stable.

FIG. 7. High frequency C - V data for MOS capacitors using TiN_x or Al gates and a 3.5 nm RPECVD SiO_2 gate dielectric. The flatband voltage shift corresponds to the work function difference between TiN_x and Al.

FIG. 8. High frequency C - V data for MOS capacitors using TiN_x or Al gates and a 2 nm RPECVD SiO_2 /2 nm RPECVD Si_3N_4 gate dielectric stack. The flatband voltage shift corresponds to the work function difference between TiN_x and Al.

minimal thickness of TiN_x was deposited to bury the interface, reducing the Si_{LVV} peak intensity to nearly zero. Only minor changes in the AES spectra for both $\text{TiN}_x/\text{SiO}_2$ and $\text{TiN}_x/\text{Si}_3\text{N}_4$ interfaces are observed below 850 °C and are most likely the result of slight variations in thickness of the TiN_x overlayer. Following the 850 °C anneal, however, the Si_{LVV} peak intensity increases substantially for the $\text{TiN}_x/\text{SiO}_2$ interface and modestly for $\text{TiN}_x/\text{Si}_3\text{N}_4$. The fact that these changes in the AES spectra occur at the same temperature for both dielectrics suggests that decomposition of TiN_x begins at 850 °C. The dramatic change in the $\text{TiN}_x/\text{SiO}_2$ interface compared to that of $\text{TiN}_x/\text{Si}_3\text{N}_4$ indicates that the metal chemically reacts with the underlying SiO_2 layer but does not interact with Si_3N_4 . The details of this reaction and the chemical structure that results, including the possible formation of a titanium silicide layer, still need to be elucidated.

High frequency C - V characteristics for MOS capacitors using TiN_x and Al gates on ultrathin RPECVD SiO_2 dielectrics are shown in Fig. 7. The flatband voltage for the TiN_x gate is shifted by $\Delta\Phi = 0.5 \pm 0.1$ eV above Al. A similar shift $\Delta\Phi = 0.4 \pm 0.1$ eV is observed in Fig. 8 for capacitors with TiN_x and Al gates on a $\text{SiO}_2/\text{Si}_3\text{N}_4$ bilayer. In each case, the flatband voltage shift results from the work function difference of the two metals. Using the known¹⁸ barrier height of 3.2 eV for Al on SiO_2 , the observed flatband voltage shift gives a barrier height of $\Phi_b = 3.7 \pm 0.1$ eV for $\text{TiN}_x/\text{SiO}_2$, in agreement with previous studies.⁸ Comparing the two devices with TiN_x gates, there is an additional flatband voltage shift $\Delta\Phi = 0.3$ eV between the capacitors using SiO_2 and $\text{SiO}_2/\text{Si}_3\text{N}_4$ dielectrics as seen in Fig. 9. This flatband voltage shift is not due to a work function difference between the contacts since the same gate metal and substrate were used in each device. Instead, this difference in flatband voltage must result from fixed positive charge in the dielectric. However, since the wafers were processed in parallel and subjected to

the same treatments at each step except for deposition of the dielectric layer, it is assumed that this fixed positive charge is intrinsic to the dielectric and does not result from device processing. The most likely source of this fixed charge is an interface dipole layer in the dielectric. Recent calculations¹⁹ suggest that dipole layers between Si/SiO_x and $\text{Si}/\text{Si}_3\text{N}_4$ interfaces may account for the observed flatband voltage shift.

IV. CONCLUSIONS

As MOS device dimensions are reduced, the impact of interface physics on their operation and performance increases dramatically. Understanding, controlling, and optimizing interface properties will be critical to continued de-

FIG. 9. Comparison of high frequency C - V curves for MOS capacitors using TiN_x gates and ultrathin SiO_2 or $\text{SiO}_2/\text{Si}_3\text{N}_4$ gate dielectrics from Figs. 7 and 8. The flatband voltage shift due to fixed charge may result from interface dipoles.

vice scaling. In particular, issues relating to the integration of novel gate dielectrics and gate metals with existing Si technology and process flows must be investigated and verified.

Metallic TiN_x gates are compatible with advanced RPECVD SiO_2 dielectric layers and $\text{SiO}_2/\text{Si}_3\text{N}_4$ dielectric stacks. TiN_x grows uniformly on these dielectrics without an intermediate seed layer. $\text{TiN}_x/\text{SiO}_2$ and $\text{TiN}_x/\text{Si}_3\text{N}_4$ interfaces are stable against chemical reaction for RTA treatments below 850 °C. At 850 °C, the metal reacts with SiO_2 possibly due to decomposition of TiN_x , but is more stable on Si_3N_4 .

MOS capacitors have been fabricated which integrate TiN_x gate electrodes with RPECVD SiO_2 or $\text{SiO}_2/\text{Si}_3\text{N}_4$ gate dielectrics and exhibit good $C-V$ characteristics. From the flatband voltage shift of the $C-V$ curves for TiN_x gates relative to Al, a barrier height of $\Phi_b = 3.7 \pm 0.1$ eV for TiN_x on SiO_2 is determined. In addition, a flatband voltage shift $\Delta\Phi = 0.3$ eV is observed between TiN_x gates on SiO_2 and $\text{SiO}_2/\text{Si}_3\text{N}_4$ gate dielectrics. This difference may result from a change in the charge dipole layer in the dielectric.

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