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Titanium–aluminum oxynitride (TAON) as high-k gate dielectric for sub-32 nm CMOS technology

J. Miyoshi [a,b,*], J.A. Diniz [a,b], A.D. Barros [a,b], I. Doi [a,b], A.A.G. Von Zuben [c]

[a] School of Electrical and Computer Engineering, University of Campinas, P.O. Box 6101, 13083-970 Campinas-SP, Brazil
[b] Center for Semiconductor Components, University of Campinas, P.O. Box 6061, 13083-870 Campinas-SP, Brazil
[c] Gleb Wataghin Institute of Physics, University of Campinas, P.O. Box 6165, 13089-970 Campinas-SP, Brazil

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High-k insulators for the next generation (sub-32 nm CMOS (complementary metal–oxide–semiconductor) technology), such as titanium–aluminum oxynitride (TAON) and titanium–aluminum oxide (TAO), have been obtained by Ti/Al e-beam evaporation, with additional electron cyclotron resonance (ECR) plasma oxynitridation and oxidation on Si substrates, respectively. Physical thickness values between 5.7 and 6.3 nm were determined by ellipsometry. These films were used as gate insulators in MOS capacitors fabricated with Al electrodes, and they were used to obtain capacitance–voltage (C–V) measurements. A relative dielectric constant of 3.9 was adopted to extract the equivalent oxide thickness (EOT) of films from C–V curves under strong accumulation condition, resulting in values between 1.5 and 1.1 nm, and effective charge densities of about 10^{11} cm^{-2}. Because of these results, nMOSFETs with Al gate electrode and TAON gate dielectric were fabricated and characterized by current–voltage (I–V) curves. From these nMOSFETs electrical characteristics, a sub-threshold slope of 80 mV/dec and an EOT of 0.87 nm were obtained. These results indicate that the obtained TAON film is a suitable gate insulator for the next generation (MOS) devices.

1. Introduction

The next generation of sub-32 nm CMOS technology requires gate insulators with a dielectric constant k higher than 40, resulting in an equivalent oxide thickness (EOT) thinner than 1 nm [1–4]. Titanium–aluminum oxide (TAO) high-k films have received considerable attention due to their electrical and physical properties, which come from the composition of titanium oxide and aluminum oxide, such as higher permittivity ($k \sim 80$) and higher band gap ($E_g \sim 8.8$ eV), respectively, than other high-k (such as HfO_2 and ZrO_2) films. Furthermore, this composition can reduce the undesirable effects on sub-32 nm MOS devices with gate dielectrics of titanium oxide or aluminum oxide, consequent of high leakage current due to the band offset of 2.8 eV of Al_2O_3 [5], and EOT higher than 2 nm due to relatively low k between 8 and 10, respectively [1]. In this work, titanium–aluminum oxynitride (TAON) and titanium–aluminum oxide (TAO) gate insulators were obtained by Ti/Al e-beam evaporation, with additional electron cyclotron resonance (ECR) plasma oxynitridation and oxidation on Si substrates, respectively. The used ECR system is downstream plasma reactor, where a separate control of ion energy and ion flux is possible. The reactor can operate at low pressures (1–50 mTorr) allowing a drastic reduction of the ion surface sputtering. A 2.45 GHz microwave source generates the plasma at high power (up to 1000 W) and a 13.56 MHz RF power source biases separately the sample chuck. The 2.45 GHz ECR source and RF chuck power control the ion flux and ion energy, respectively, allowing low temperature, low pressure and low damage chemical vapor deposition (CVD) or plasma Si surface oxidation and/or nitridation [6].

It is important to notice that, to the best of our knowledge, there are no reports in the literature regarding titanium–aluminum oxynitride (TAON) films as MOS gate dielectric [1–4]. The nitrogen incorporation in TAO can reduce Al diffusion into the Si substrate [7].

2. Experimental procedures

Titanium–aluminum oxynitride (TAON) and titanium–aluminum oxide (TAO) layers were formed on p-type Si (1 0 0) wafers. The substrates were cleaned with a standard RCA method [8]. About 0.5 nm titanium (Ti) and 0.5 nm aluminum films were subsequentially deposited on Si substrates by vacuum e-beam evaporation of 99.9999% of Ti and Al metals, respectively, without any substrate heating. The evaporation pressure was 3×10^{-8} Torr, and the Ti and Al evaporation rates were of 0.1 nm s^{-1}. ECR plasma oxidation and oxynitridation processes were carried out at

* Corresponding author. Address: School of Electrical and Computer Engineering, University of Campinas, P.O. Box 6101, 13083-970 Campinas-SP, Brazil.
E-mail address: julianamiyoshi@gmail.com (J. Miyoshi).

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different O_2:N_2:Ar flow ratios (13:0:20 sccm and 3:10:20 sccm, respectively). These samples were named, respectively, TAO and TAON-1. The substrate temperature, process pressure, 2.45 GHz ECR power and 13.56 MHz rf power were fixed at 20 °C, 5 mTorr, 750 W, and 0 W, respectively. Metal/AlTi(oxide or oxynitride)/Si capacitors were formed with Al (300 nm) gate electrodes, which were deposited by DC sputtering deposition, sintered in conventional furnace in forming gas at 450 °C for 15 min. The electrodes were patterned with a mask composed of an array of 200 μm diameter dots.

Also, enhancement nMOSFETs (with TAON as gate dielectric) were fabricated on p-type single-crystal Si (1 0 0) wafers with resistivity ranging from 1 to 10 Ω cm. These devices with an area of 32 μm × 8 μm were defined with five lithography steps. Boron ion implantation (65 keV $^{11}B^+$ ions and dose of 3×10^{13} ions/cm^2) and dopant activation annealing (1000 °C for 20 min in N_2) were performed to adjust the threshold voltage. The substrates were cleaned by RCA method between each process step and were oxidized (1000 °C for 280 min in $O_2 + H_2O(v)$) to grow a 1 μm field silicon oxide. Phosphorus ion implantation (80 keV P^+ ions and dose of 7×10^{15} ions/cm^2) and dopant activation annealing (1000 °C for 30 min in N_2) were used for the formation of source and drain junctions. The samples for nMOSFETs were identified as TAON-2**,** because, the used TAON dielectric gate was obtained, as follows: 0.75 nm titanium (Ti) and 0.25 nm aluminum subsequentially deposited on Si substrates by vacuum e-beam evaporation of 99.9999% of Ti and Al metals, respectively, without any substrate heating. The evaporation pressure was 3×10^{-8} Torr, and Ti and Al evaporation rates 0.1 nm s^{-1}. The ECR plasma oxynitridation process was carried out at O_2:N_2:Ar flow ratio of 3:10:20 sccm. After the gate insulator formation, 300 nm thick aluminum was deposited by DC sputtering process to form the MOS structure top contacts. Then, following the process steps, the wafer backside was etched in buffered HF and a 300 nm thick Al film was evaporated. Finally, Al contact sintering was performed at 450 °C in forming gas.

Chemical bonding characteristics of the titanium–aluminum oxynitride (TAON) and titanium–aluminum oxide (TAO) films were evaluated using FTIR (Fourier transform infrared spectroscopy). The film thickness values were determined by ellipsometry. MOS capacitors were used to obtain capacitance–voltage (*C–V*) and current–voltage (*I–V*) measurements. A relative dielectric constant of 3.9 (for silicon oxide film) was adopted to extract the equivalent oxide thickness (EOT) of films from *C–V* curves. Gate leakage current densities were extracted by current–voltage (*I–V*) measurements. nMOSFETs with Al gate electrode and TAON gate dielectric were characterized by *I–V* curves.

3. Results and discussion

FTIR spectra of the control silicon oxide (CO), control silicon oxynitride (CON), titanium–aluminum oxide (TAO) and titanium–aluminum oxynitride (TAON-1) films are shown in Fig. 1. From the spectra of control CO and CON, absorption peaks at 1064 and 1051 cm^{-1} (stretching mode), respectively, due to Si–O bonds in silicon oxide are observed. Due to the presence of nitrogen in the film, peak position is shifted to lower values [9], and the lower the wavenumber, the higher the nitrogen content in the oxynitride film. This result indicates that CO and CON films are silicon oxide and oxynitride, confirming the ECR plasma oxidation and oxynitridation on Si surfaces. In the TAO and TAON-1 film spectra, absorption peaks at 1105 and 1107 cm^{-1}, respectively, can be attributed to Si–O and/or O–Al–O bonds [9,10], which confirms the plasma oxidation on Al/Ti/Si structures. Furthermore:

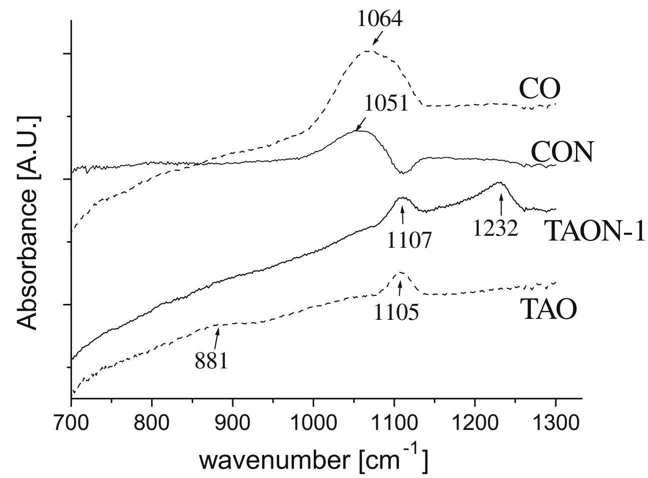

Fig. 1. FTIR spectra of the control silicon oxide (CO), control silicon oxynitride (CON), titanium–aluminum oxide (TAO) and titanium–aluminum oxynitride (TAON-1) films.

- as absorption peak at 1232 cm^{-1} are related to Si–O and/or O–Al–N bonds, the aluminum oxynitride formation occurred in the TAON-1 samples [10].
- as absorption peak at 881 cm^{-1} are related to Al_2O_3 layer formation, the aluminum oxide formation occurred in the TAO samples [11].
- as Si–O bonds were observed, probably, $(Ti_wAl_xO_yN_z)/SiO_x$/Si and $(Ti_wAl_xO_y)/SiO_x$/Si structures were formed.
- These TAO and TAON-1 films are thinner than 10 nm (this result was confirmed by ellipsometry). Thus, lower intensity peaks, such as the absorption peak at 480 cm^{-1}, which are related to Ti–O bonds, were not identified in the FTIR spectra [11].
- For more details about $Ti_wAl_xO_yN_z$ and $Ti_wAl_xO_y$ film compositions, SIMS, XPS, HRTEM and AFM analyses are presently underway.

Film thicknesses were measured by ellipsometry using a fixed wavelength of 632.8 nm and an incidence angle of 70°. It needs to be remarked however, that ellipsometry measurements are not very confident for ultra-thin films (thinner than 10 nm), and to measure the thickness of these films, the refractive index must be fixed. A refractive index of 1.46 (for thermal silicon oxide) was applied for control silicon oxide (CO) and control silicon oxynitride (CON) films, because these dielectrics are based on silicon oxide. Physical thickness values of 8.7 and 4.6 nm, respectively, for CO and CON films were thus obtained. Two different refractive indexes of 1.64 (for Al_2O_3) and 2.42 (for TiO_2) were applied for titanium–aluminum oxide (TAO) and titanium–aluminum oxynitride (TAON-1) films, because these dielectrics are based on the mixture of aluminum oxide and titanium oxide. TAO and TAON-1 thickness values are about 6.3 and 5.8 nm for both fixed refractive indexes of 1.64 (for Al_2O_3) and 2.42 (for TiO_2), respectively. These thickness values for TAO and TAON-1 films will be used in the *C–V* analysis to determine the dielectric constant *k*. Furthermore, these values indicate that films were grown on Si substrates by plasma oxidation or oxynitridation of Al (0.5 nm) and Ti (0.5 nm) stack layers and agrees with the FTIR results.

The 1 MHz *C–V* and *I–V* characteristics of Al/CO/Si, Al/CON/Si, Al/TAO/Si and Al/TAON-1/Si specimens were experimentally obtained using Keithley model 590 *C–V* and 4200 SCS analyzers, respectively. Figs. 2 and 3 present *C–V* characteristics of the MOS capacitors with gate dielectrics based on Ti/Al (TAO and TAON-1) and with control gate dielectrics (CO and CON), respectively. The