A comparative study of anodic tantalum pentoxide and high-pressure sputtered titanium oxide

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In this work we present a new method to fabricate improved TiO_2 films by using a high-pressure sputtering system. In order to minimize the damage induced in the substrate surface by the ion bombardment, a high chamber pressure of 100 Pa is used, which is very much higher than typical values in conventional systems. We present results obtained by X-ray diffraction and FTIR spectroscopy. Moreover, we will compare the properties of the resulting TiO_2 -insulator-metal capacitors with those of anodic Ta_2O_5 . Very thin films of TiO_2 have been obtained with a very promising quality for future electron device fabrication.

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1. Introduction

Development of high-density MOS dynamic random-access memory (DRAM) devices with small cell areas has been accomplished by reducing the thickness of the SiO_2 storage capacitors to maintain the required charge storage level. However, the reduction of the SiO_2 insulator thickness is going to approach the physical limit. The microelectronics roadmap requires new high- k dielectrics to replace silicon oxide in future ULSI generations. Presently, many ultra-large-scale-integration (ULSI) research laboratories are aiming their efforts at the production of very thin insulator films equivalent to nanometer-scale SiO_2 films with a leakage current density less than $10^{-8} \text{ A cm}^{-2}$ at the ULSI supply voltage.

Tantalum pentoxide ($\epsilon_r = 25$) has been investigated as one of the most promising materials for capacitor fabrication. Recently, we reported good-quality Ta_2O_5 films fabricated by using a very inexpensive technique: anodization of tantalum silicide and tantalum nitride precursors. In previous studies we presented a fabrication method of thermally stable anodic Ta_2O_5 MIM capacitors [1,2]. We investigated the influence of different technological parameters on the capacitor performances. We studied the conduction mechanisms in our dielectric films. Modified and standard Poole–Frenkel effects appear as the main conduction mechanisms responsible for conduction in the capacitors. Finally, we observed by transmission electron microscopy (TEM) and Auger electron spectroscopy (AES) that Ta_2O_5 films actually consist of two layers: the lower one, just above the substrate, containing nitrogen and the upper one with no nitrogen content.

Recently, we observed the existence of conductance transients for different conditions of voltage bias amplitude, frequency, and temperature [3,4]. We obtain supplementary information on the physical nature of anodic tantalum pentoxide thin films. Several relaxation mechanisms occur in the dielectric. At frequencies in the range of 100 kHz cathodic pulse bias induces relaxation processes related to the molecular orientation inside the dielectric. Moreover, the electric field produces displacements in interface charged traps that give rise to the slowest component of the conductance transients. This must be related to some absorption peak occurring at frequencies close to 100 kHz. Relaxation processes occurring at these frequencies are typically related to the orientation of dipoles caused by the applied electric field.

Titanium oxide is another challenger to replace silicon dioxide. TiO_2 films obtained by different techniques show dielectric constant values of around 70–80, that is, 20 times higher than SiO_2 . Many different process techniques have been tried to obtain good TiO_2 films (CVD, d.c. and r.f.-sputtering, etc.) [5–8]. However, poor electrical properties have been reported in terms of leakage currents, breakdown voltages, etc. This poor behavior can be caused by structural defects in the oxide, damage produced on the substrate surface during the process, chemical reactions between the different species present in final structures, etc. It is experimentally established that the structure, phase composition, and electrical properties of TiO_2 films are very sensitive to deposition conditions. In this work, we present a new method to fabricate improved TiO_2 films by using a high-pressure sputtering system.

2. Sample fabrication

2.1. Anodic tantalum pentoxide capacitors

For the fabrication of tantalum oxide capacitors, TaN_x and Al-TaN_x films have been deposited on silicon wafers by d.c. magnetron reactive sputtering. Varying the N_2/Ar flow ratio during sputter deposition has varied the nitrogen content of the TaN_x films between 8 and 33 at %. All samples fabricated on Al-TaN_x underwent thermal anneals at 350°C for 1 h. The anodization is performed as follows: wafers are immersed in a 0.01 wt % citric acid solution and act as the anode of a circuit where a Pt electrode is used as the cathode. The anodization voltages ranged from 5 to 230 V, with a soak time of 1 h. The growth rates are about $1.6\text{--}2\text{ nm V}^{-1}$ and the film thickness ranges from 10 to 450 nm. In this way, we have fabricated very thin film capacitors with an equivalent silicon dioxide thickness (EOT) as low as 1.7 nm, having leakage density currents less than 10^{-6} A cm^{-2} . This means that we have fabricated capacitors with capacitance densities as high as $20\text{ fF }\mu\text{m}^{-2}$. Atomic force microscopy and SEM cross-sectional images of these films show typical rms roughness values of around 3 nm.

2.2. High-pressure sputtered titanium dioxide capacitors

Titanium dioxide thin films were grown in a high-pressure sputtering system. In order to minimize the damage induced in the substrate surface by the ion bombardment, high chamber pressure values were used. TiO_2 films were deposited on (1 1 1) silicon substrates by sputtering in an oxygen atmosphere at a pressure of 100 Pa, which is very much higher than typical values in conventional systems. We used a 3.5-cm diameter target of ceramic TiO_2 . The plasma power was 60 W and three sets of samples were fabricated at different substrate temperatures: 200, 400 and 600°C . The deposition time was 4 h for all the samples. Subsequently, samples were submitted to rapid thermal anneals at different temperatures. The thicknesses of these films were about 10 nm.

3. Experimental

3.1. R.F.-impedance analysis setup

Impedance analysis has been carried out by measuring equivalent series resistance and capacitance values as a function of the frequency. For low and intermediate frequencies (40 Hz–110 MHz) we have used an Agilent 4280A Impedance Analyzer and for high frequencies (1 MHz–3 GHz) we used an Agilent 4287A LCR Analyzer. These instruments use the I – V method [9] to carry out impedance measurements. The impedance is calculated from measured voltage and current values. Current is calculated using the voltage measurement across an accurately known low-value resistor, R . In practice, a low-loss transformer is used in place of R to prevent the effects caused by placing a low-value resistor in the circuit. This method provides more reliable values than others commonly used in r.f. when measuring unknown impedance values. For instance, the network analysis method provides very poor accuracy when the measured impedance is much lower or higher than the characteristic impedance.

3.2. Anodic tantalum pentoxide MIM capacitors

When capacitors are biased, impedance measurements noticeably change with respect to zero bias. Fig. 1 shows “as-measured” equivalent series capacitance and resistance for different values of the voltage bias. These curves correspond to 20 V anodized capacitors. We also see that curves are different depending on the sign of the applied voltage. Anodic bias means that the electric field direction in the oxide is the same as during anodizing, whereas during cathodic conditions it is just the opposite. We observe an asymmetric behavior between them. We interpret this asymmetry in terms of the anodic nature of the insulator: after fabrication, tantalum oxide molecules are oriented along a preferred orientation because of the anodization field. When applying an opposite electric field variation molecules are reoriented giving rise to a change in the dipolar moment, whereas anodic pulses do not produce any change.

In Fig. 2a we plot capacitor loss tangent curves at room temperature and several voltages. We observe that at low frequencies the loss tangent increases noticeably for cathodic voltages, whereas this effect does not appear for anodic voltages. Fig. 2b shows that this effect is more apparent for high temperatures. These results reveal that the effect responsible for the increase of the conductivity of tantalum oxide at low frequencies is both electrically and thermally activated.

We explain these results as follows: Anodic Ta_2O_5 films actually consist of two dielectric layers with an

Figure 1 Equivalent series capacitance of Ta_2O_5 capacitors for (a) anodic and (b) cathodic bias.

Figure 2 (a) Loss tangent versus voltage curves for anodic tantalum pentoxide at room temperature, (b) Loss tangent at cathodic voltage for anodic tantalum pentoxide at several temperatures.

interlayer between them (Fig. 3). Because traps existing in the interlayer have a time constant of about 0.3 μ s, the frequency response of the capacitors vanishes at frequencies higher than 3 MHz. Impedance curves obtained under anodic and cathodic bias conditions reveal that these capacitors have to be modeled as a triple capacitance in parallel with a conductance for the three layers of the dielectric. Moreover, a contact resistance term has to be included in the model. Leakage resistance, as a function of the voltage bias, exhibits the

Figure 3 AES spectrum for a Ta_2O_3 film grown by TaN_x anodization revealing the existence of two layers.

Figure 4 FTIR spectra for high-pressure sputtered TiO_2 films on silicon substrates.

asymmetrical behavior typically shown by anodic dielectrics.

3.3. High-pressure sputtered titanium oxide

The titanium oxide films were studied by X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR). No differences have been observed between the XRD spectra of original and sputtered substrates, indicating that the TiO_2 films are amorphous.

As for the FTIR results, in Fig. 4 we show the spectra of TiO_2 films annealed at a temperature of 1000 $^{\circ}\text{C}$. In the low-frequency region of the spectrum, the TO phonon band appears at 436 cm^{-1} . This is in agreement with the Gonzalez *et al.* [10, 11] data on the TO phonon modes of the nanocrystalline titania. When the same film was annealed to 1000 $^{\circ}\text{C}$, in addition to the 436 cm^{-1} band, a new band developed at 490 cm^{-1} . This band may correspond to the TP phonon frequency of TiO_2 in the rutile phase. This indicates that a very high temperature annealing has to be used in order to obtain crystalline structures. In this figure we can clearly see a peak at a frequency of 1060 cm^{-1} corresponding to the Si-O band. In the inset we observe that this peak increases with annealing temperature, indicating the formation of a good-quality silicon oxide buffer layer on the silicon substrate. In Fig. 5 we plot the Si-O peak area for all the

Figure 5 Si-O peak area as a function of RTA temperature.

Figure 6 R.f. impedance curves of high-pressure sputtered TiO_2 films; (a) capacitance, (b) conductance.

samples. These results prove that the SiO_2 layer thickness increases with the annealing temperature.

Fig. 6 shows the electrical characteristics of Ag- TiO_2 -Si devices fabricated with these films. Although these curves are very preliminary, we can see that capacitance (Fig. 6a) and conductance (Fig. 6b) vary with temperature and electric field. These suggest that several conduction mechanisms are involved, including thermal-activated and field-dependent phenomena.

4. Conclusions

This study, for the first time, applies the r.f. impedance analysis (RFIA) method to anodic tantalum pentoxide capacitors. Anodic Ta_2O_5 films actually consist of two dielectric layers with an interlayer between them. Because traps existing in the interlayer have a time

constant of about $0.3 \mu\text{s}$, the frequency response of the capacitors vanishes at frequencies higher than 3 MHz. Impedance curves obtained under anodic and cathodic bias conditions reveal that these capacitors have to be modeled as a triple capacitance in parallel with a conductance for the three layers of the dielectric. Moreover, a contact resistance term has to be included in the model. Leakage resistance as a function of the bias voltage exhibits the asymmetrical behavior typically shown by anodic dielectrics.

As for titanium oxide, XRD spectra reveal that high sputtered TiO_2 films are amorphous. Absorption infrared spectra show that, in the low-frequency region of the spectrum, the TO phonon band appears at 436 cm^{-1} . Moreover, we observe a peak at a frequency of 1060 cm^{-1} corresponding to the Si-O band. This peak increases with annealing temperature, indicating the formation of a good-quality silicon oxide buffer layer on the silicon substrate. The SiO_2 layer thickness increases with the annealing temperature. The electrical characteristics of Ag- TiO_2 -Si devices fabricated with these films suggest that several conduction mechanisms are involved, including thermal-activated and field-dependent phenomena.

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