In this article, we investigate the frequency-dependent voltage nonlinearity effect of high-κ Ni/SrTiO3/TaN and TaN/SrTiO3/TaN radio-frequency (rf) metal-insulator-metal (MIM) capacitors by electrical and thermal stresses. The experimental results demonstrated that the MIM-related capacitance properties, dependence of voltage and frequency, are not only affected by intrinsic dielectric properties but also shared by extrinsic effect, which possibly originated from the oxygen vacancies or electrode polarization. The high work-function Ni electrode can prevent the frequency-dependent voltage coefficient of capacitance characteristics from deterioration under the high temperature or continued voltage-stressing environments.

© 2010 The Electrochemical Society. [DOI: 10.1149/1.3491490] All rights reserved.

Manuscript submitted April 19, 2010; revised manuscript received August 2, 2010. Published September 25, 2010.

The SrTiO3 (STO) metal-insulator-metal (MIM) capacitors with a high dielectric constant of >50 show the potential for the radio frequency (rf)/analog application. However, the high annealing temperature of >450 °C for nanocrystal formation exceeds the maximum temperature (<400 °C) permitted for back integration. Although STO, TiO2, and ZrO2 dielectrics with crystallized phase own a higher capacitance density for equivalent oxide thickness scaling, large leakage current via grain boundary and poor voltage nonlinearity are other concerns. The crystallized dielectrics may lead to the low breakdown voltage and reliability issue, which originate from the grain boundaries to weaken breakdown strength. In addition, the oxygen vacancies or mobile charges in n-type STO dielectrics play an important role in the variations of voltage coefficient of capacitance (VCC). The VCC characteristics are not only dominated by the intrinsic properties of the dielectric but are also influenced by mobile oxygen vacancies near the interface between the dielectric and electrodes. Fortunately, the leakage current and VCC characteristics can be improved further by work-function tuning.

However, up to now, the frequency-dependent VCC characteristic of the STO MIM capacitor is rarely discussed even though many papers of MIM capacitors have been reported. In this work, the frequency-dependent capacitance characteristics were extensively investigated by elevated temperature-bias stressing in the amorphous STO MIM capacitors with Ni and TaN electrodes. The high work-function Ni not only suppresses thermal-induced leakage current effectively but also improves the VCC characteristics under high temperature and continued stress environments. Furthermore, the point to observe is the frequency-dependent VCC characteristics, mainly governed by the extrinsic contribution from space charge relaxation rather than an intrinsic dielectric.

Experimental

After depositing 2 μm SiO2 on Si wafer, a lower capacitor electrode was formed using physical vapor deposition TaN/Ta bilayers. After patterning the bottom electrode, TaN was treated by NH3 plasma nitridation. Then the 25 nm thick STO were deposited on the TaN/Ta electrode by a sputtering with a mixing gas of Ar/O = 5/1, followed by 400 °C post deposition annealing for 30 min under oxygen environment. Finally, the TaN and Ni metal were deposited and patterned to form the top capacitor electrode. The fabricated MIM capacitors were characterized using an HP4284A precision LCR meter to 1 MHz and an HP8510C network analyzer for the S-parameter measurements to 5 GHz.

Results and Discussion

Figure 1a and b shows the capacitance–voltage (C–V) characteristics of STO MIM capacitors measured from 100 kHz to 10 GHz. In Fig. 1a, the capacitance densities of 17 and 18.8 fF/μm² are measured at 1 MHz for Ni/STO/TaN and TaN/STO/TaN MIM capacitors, respectively. The ~9.5% difference in the capacitance density, based on the space charge theory, may be due to the increase of space charge capacitance caused by higher work-function Ni. Also, the excess space charges between the electrodes and STO dielectrics may contribute to an unwanted frequency dispersion due to the discrepancy of relaxation time in low and high frequency, as shown in Fig. 1b. In addition to the work-function difference of metals, one possible reason to explain the larger frequency dispersion of TaN than that of Ni is due to ion damage on STO during top TaN deposition by sputtering. In the insert of Fig. 1a, the leakage current of 4.7 × 10⁻⁹ A/cm² at ~1 V for Ni/STO/TaN MIM capacitor is much lower than that of TaN/STO/TaN by ~2.5 order of magnitude. Therefore, the selectivity of the work function of the electrode is very important for the STO dielectric with a narrow bandgap (~3.3 eV) and small conduction band offset (ΔEg ~ 0).

Another point we need to consider is that the STO probably became a defect-rich film as the dielectric failed to be activated completely due to a limit of back end process integration. The oxygen vacancies can be a main issue to cause the capacitance variation or frequency dispersion, except for large leakage current. As shown in Fig. 1c, the as-deposited STO exhibits a resistive switching behavior, possibly resulting from oxygen vacancies in the bulk. The nonstoichiometric SrTiO3 film with resistive switching behaviors through conductive filaments, consisting of oxygen vacancies, presents the capacitance switching behaviors with frequency dependence of capacitance.

Therefore, we use the VCC model based on an electrode polarization mechanism reported recently to investigate the phenomena of frequency-dependent capacitance variation. The electrode polarization mechanism implied that mobile charges form an accumulation layer at electrodes, leading to a voltage-dependent double layer capacitance to affect the frequency dispersion. The model can be expressed as

\[ C = C_m + \frac{1}{1 + \omega^2 \tau^2} \]

where \( C_m \) is the capacitance in the absence of electrode polarization, \( C_m = \frac{e_0\varepsilon_r A}{t_{ox}} \), \( A \) is the area of top metal, \( t_{ox} \) is the film thickness.
means that the Debye response and n is inserted in data from 0.2 to 5 GHz are obtained from the S-parameters. The capacitance density at 0 V. The rapid frequency dispersion and the frequency-dependent capacitance density of VCC and temperature dependent coefficient (TCC) characteristics are shown in Fig. 3. The VCC-TE case. Furthermore, the TCC value of TaN electrode. The high work-function Ni with a higher barrier lower than the TaN/STO/TaN capacitor characteristics are shown in Fig. 3. The VCC-TE case. Furthermore, the TCC value of 2630 ppm °C for Ni is also much smaller than 4880 ppm °C for the TaN electrode. The high work-function Ni with a higher barrier height (φb) can increase the relaxation time of mobile charges and hence improve the voltage nonlinearity (ΔC/C0).

As for other related capacitor properties, the temperature dependence of VCC and temperature dependent coefficient (TCC) characteristics are shown in Fig. 3. The VCC-a values of 3460 and 2630 ppm/V² at 500 kHz for TaN and Ni top electrode (TE) cases were obtained, respectively, which can also be improved rapidly with a decreased capacitance density. The VCC-a for the Ni TE case shows a linearly reduced trend but a polynomial temperature dependence for the TaN TE case. Furthermore, the TCC value of 465 ppm/°C for Ni is also much smaller than 4880 ppm/°C for the TaN electrode. The high work-function Ni with a higher barrier height than TaN can lower the effects of carrier injection or trap relaxation corresponding to TCC value at elevated temperatures. Therefore, the high work-function Ni can reduce the thermal impact on the capacitor characteristics of VCC and TCC for the small ΔEc STO.

To further understand the influence of electrode material on frequency dispersion and the ΔC/C0, the STO MIM capacitors are stressed by a constant voltage stress (CVS) approach and then measured by the range from 100 kHz to 5 GHz. The devices during voltage stressing at a bias of −4 V is plotted in Fig. 4a. Here, the ΔC/C0 represents the value of C(−2 V) − C0/C0, where C0 is the capacitance density at 0 V. The rapid ΔC/C0 reduction with frequency is attributed to the trapped carriers being unable to follow
Figure 3. $C/C_0$ dependence of temperature and TCC characteristic of STO MIM capacitors.

Figure 4. (Color online) (a) Frequency dependence of $C(f)/C_{100\ kHz}$ and $\Delta C/C_0$ and (b) VCC-\(\alpha\) as a function of stress time by CVS at -4 V. The conduction mechanisms fitted at low and high electrical fields are inserted in (a).

Figure 5. (Color online) Frequency dependence of $C(f)/C_{100\ kHz}$ and $\Delta C/C_0$ by temperature-bias stress.

Conclusions

The oxygen vacancies play an important role for high frequency rf capacitors, possibly as active mobile carriers or bulk traps which affect the analog characteristics (VCC or TCC). Therefore, it is believed that frequency-dependent VCC characteristics may be dominated by extrinsic capacitance, depending on the relaxation of trap charges, rather than the intrinsic one.
Acknowledgment

This work was supported in part by the National Science Council of Taiwan.

References