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Extended Abstracts of the 2013 International Conference on Solid State Devices and Materials, Fukuoka, 2013, pp852-853

Impact of Plasma Nitridation on Reliability Performance of MIM Capacitors Based on $ZrLaO_x/ZrTiO_x/ZrLaO_x$ Laminate Insulator

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I. Introduction

Metal-insulator-metal (MIM) capacitors are very attractive for radio frequency (rf) and analog/mixed signal circuits. Although MIM capacitors with capacitance density higher than 20 fF/μm^2 have been accomplished by many high-permittivity (high-κ) dielectrics such as $SrTiO_3$ [1], TiLaO [2], TiO_2 [3], Nb_2O_5 [4] and crystalline-ZrO_2 [5-6], a feasible MIM for circuit applications should also possess a low quadratic voltage coefficient of capacitance (VCC-α) which is an important indicator to evaluate how capacitance changes with applying voltage. A direct avenue to achieve a low VCC-α is to suppress leakage current by increasing dielectric thickness. However, it comes at the price of lower capacitance density. Recently, a promising approach that could concurrently obtain a high capacitance density without sacrificing VCC-α was proposed by depositing two dielectrics which respectively possesses a positive and negative VCC-α value and therefore the so-called "canceling effect" can be achieved [7]. Since SiO_2 is a well-known dielectric with a negative VCC-α and therefore various dielectric stacks such as HfO_2/SiO_2 [7], Sm_2O_3/SiO_2 [8], and crystalline-TiO_2/SiO_2 [9] have been reported. One intrinsic limitation of these dielectric stacks is the relatively low κ value that makes capacitance density difficult to be further enhanced. Aiming at the limitation, an innovative high-κ dielectric $ZrTiO_x$ (κ~22.5) with an exceptional negative VCC-α was developed. By integrating $ZrLaO_x$ which shows a positive VCC-α, MIM capacitors with $ZrLaO_x/ZrTiO_x/ZrLaO_x$ stack [10] could achieve a high capacitance density of 14.60 fF/μm^2 and a low VCC-α of 33 ppm/V^2, which concurrently meet ITRS requirement of capacitance density (>12 fF/μm^2) and VCC-α (<100 ppm/V^2) set for 2020. Based on the promising electrical characteristics, reliability performance was investigated in this work and how the plasma nitridation affects the reliability was also explored. In fact, although plasma nitridation has been shown to have beneficial effect on VCC-α improvement and leakage reduction for Sm_2O_3 [11] and crystalline-TiO_2/SiO_2 [12], its effect on reliability has never been studied. With proper plasma nitridation on $ZrTiO_x$, MIM capacitors show slightly degraded capacitance density of 14.38 fF/μm^2 and VCC-α of 68 ppm/V^2 which still meet ITRS requirement. Nevertheless, plasma nitridation exhibits greatly improved leakage current by a factor of 32.8. In addition, low stress induced leakage current (SILC) of 0.16 under 2.5 V for 1000 sec and nearly frequency-independent capacitance can be achieved. Most importantly, with the same stress field, good reliability in terms of 0.38 % capacitance change after 10-year operation is also accomplished.

II. Experiment

500-nm SiO_2 on Si was used as the starting material for MIM capacitors to simulate backend process. MIM capacitors were formed by first depositing 200-nm TaN metal layer as the bottom electrode. Then the dielectric of 5-nm $ZrLaO_x$/5-nm $ZrTiO_x$/5-nm $ZrLaO_x$ was sequentially deposited by electron beam evaporation. Afterward, 400 ^oC O_2 annealing was performed to enhance the film quality. For some devices, additional 50-W N_2 plasma nitridation for 60 and 120 sec at 250 ^oC was carried out on $ZrTiO_x$ to understand how nitrogen incorporation affects reliability performance. Finally, TaN metal layer of 200 nm was deposited and patterned with a size of 250 μm×250 μm as the top electrode.

III. Results and Discussion

Fig. 1 shows the dependence of zero-biased capacitances (C_0) and VCC-α on various nitridation conditions for MIM capacitors. For devices without nitridation, the capacitance is 14.60 fF/μm^2 and it slightly decreases to 14.38 and 14.22 fF/μm^2 with 60-sec and 120-sec nitridation respectively. The decrease of capacitance with nitridation time can be explained by the smaller permittivity for nitrided $ZrTiO_x$ as compared to untreated $ZrTiO_x$. The change in permittivity with nitrogen incorporation is consistent with the behavior of TiO_2 [12] and ZrO_2 [13]. In addition, nitridation also makes a larger VCC-α with nitridation time. This trend is reasonable since nitrogen radicals could passivate oxygen vacancies in the $ZrTiO_x$ during plasma treatment and therefore nitrided $ZrTiO_x$ is expected to have a less negative VCC-α. Because of the "canceling effect", a less negative VCC-α from nitrided $ZrTiO_x$ would make the effective VCC-α of the whole dielectric stack become more positive. Note that even plasma nitridation slightly degrades both capacitance density and effective VCC-α, the data of 14.38 fF/μm^2 with 68 ppm/V^2 for devices with 60-sec nitridation time still meets the requirements set by 2020 ITRS and therefore 60-sec nitridation is adopted in the following discussion. **Fig. 2** and **Fig. 3** respectively show the impact of nitridation on current-voltage (I-V) characteristics measured at 25 ^oC and 85 ^oC. It is obvious that leakage current can be greatly reduced by a factor of 32.8 and the improved leakage performance can be explained by the suppressed oxygen vacancies mediated leakage paths due to reduced gap states by nitrogen incorporation [14]. **Fig. 4** demonstrates that Schottky emission is the conduction mechanism for devices with and without nitridation and the effective barrier height increases with nitridation. **Fig. 5** shows the temperature dependence of $\Delta C_{temp}/C_0$ where C_0 denotes the zero-biased capacitance at 25 ^oC and ΔC_{temp} is the difference between zero-biased capacitances at a specific temperature and C_0. With plasma nitridation to decrease the amount of oxygen vacancies and consequently make higher relaxation time (τ), temperature coefficient of capacitance (TCC) improves from 96 ppm/^oC to 65 ppm/^oC. **Fig. 6** shows the stress induced leakage current (SILC) under 2.5 V or 1.67 MV/cm for devices with different process conditions. SILC is defined by $(J_{1000}-J_0)/J_0$ where J_0 and J_{1000} respectively denotes the current before stress and after 1000-sec stress. With nitridation, SILC of 1000 sec at +1 V can be improved from 1.7 to 0.16 due to less oxygen vacancies which makes less trap generation during electrical stress. **Fig. 7** demonstrates how nitridation affects the frequency-dependent capacitance which arises from oxygen vacancies induced mobile charges for devices after stressing at 2.5 V for 1000 sec. Since nitrogen radicals effectively passivate oxygen vacancies and greatly decrease the trap generation rate during stress, nitrided devices exhibit much more stable capacitance against measurement frequency. Illustrated in **Fig. 8** is the dependence of $\triangle C_{stress}/C_0$ on constant voltage stress (CVS) time where $\triangle C_{stress}$ is the difference between fresh and stressed C_0. The capacitance increase over stress time and this result can be ascribed to a modulated permittivity caused by the trapped charges and consequent generation of dipoles during stress. The extrapolated $\triangle C_{stress}/C_0$ for 10-year lifetime from Fig. 8 as a function of stress voltage is shown in **Fig. 9**. Apparently, with 2.5 V CVS, devices without nitridation exhibit a larger $\triangle C_{stress}/C_0$ of 1.72 % after 10 years while those with nitridation demonstrate a well-controlled capacitance variation with 0.38 %.

IV. Conclusion

Through appropriate plasma nitridation of $ZrTiO_x$, although capacitance and VCC-α slightly degrade to 14.38 fF/μm^2 and 68 ppm/V^2, MIM capacitors with $ZrLaO_x/ZrTiO_x/ZrLaO_x$ laminate still meets ITRS requirements set for 2020. The major benefits gained from plasma nitridation are the greatly improved electrical characteristics and reliability performance in terms of much reduced leakage current by a factor of 32.8, SILC of 0.16 and near frequency-independent capacitance after stress. Furthermore, desirable reliability of 0.38 % capacitance change after 10-year operation under 2.5 V stress is also accomplished. These eminent results suggest that nitrided $ZrTiO_x$ makes $ZrLaO_x/ZrTiO_x/ZrLaO_x$ laminate more feasible for advanced circuit applications.

Acknowledgements

This work was supported by the National Science Council of Taiwan under contract NSC 101-2628-E-007-012-MY3 and NSC 101-2120-M-009-004.

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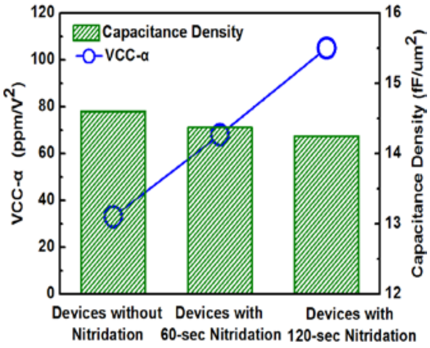

Fig. 1 Dependence of plasma nitridation time on capacitance density and VCC-α.

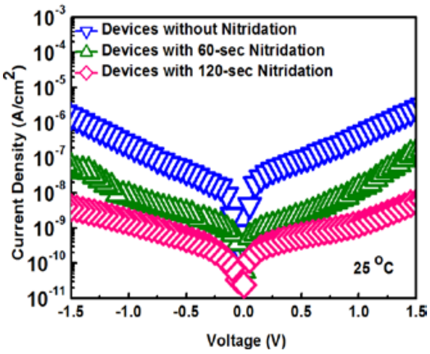

Fig. 2 I-V characteristics measured at 25 °C for devices with different process conditions.

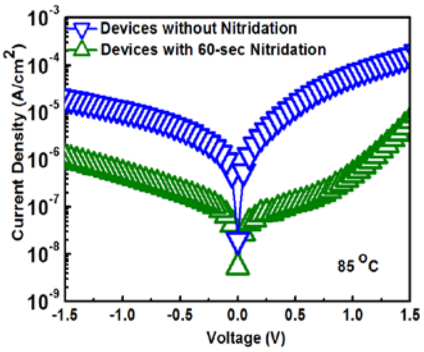

Fig. 3 I-V characteristics measured at 85 °C for devices with different process conditions.

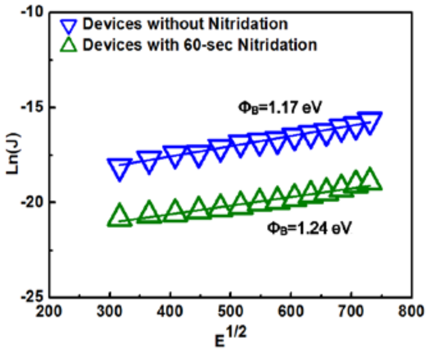

Fig. 4 Comparison of Ln(J) vs. $E^{1/2}$ characteristics for devices with different process conditions.

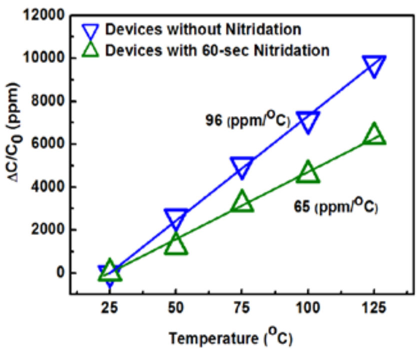

Fig. 5 Temperature dependence of $\Delta C_{temp}/C_0$ for capacitors with different process conditions

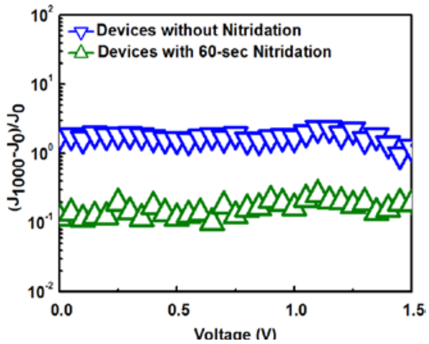

Fig. 6 Impact of plasma nitridation on SILC.

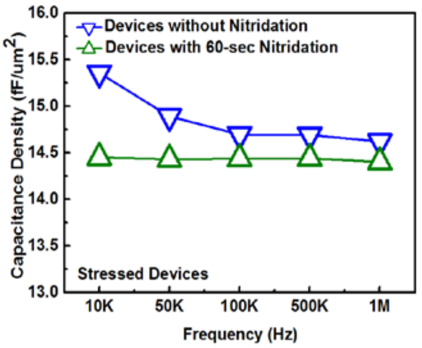

Fig. 7 Capacitance density versus measurement frequency for stressed devices with different process conditions.

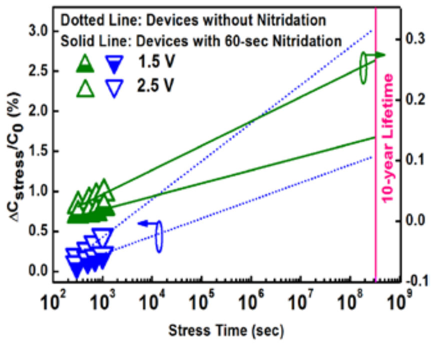

Fig. 8 Dependence of $\triangle C_{stress}/C_0$ on constant voltage stress time measured at room temperature for different process conditions.

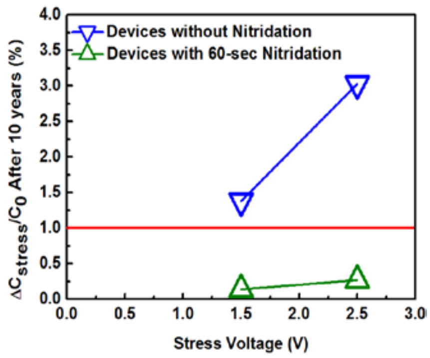

Fig. 9 Dependence of extrapolated $\triangle C_{stress}/C_0$ for 10-year lifetime on stress voltage for different process conditions.