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Improved Leakage Current for TiO_2-Based MIM Capacitors by Embedding Ge Nanocrystals

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I. Introduction

Metal-insulator-metal (MIM) based capacitors have been recently perceived as feasible passive components for radio frequency (RF), analog and mixed signal integrated circuits. With the advent of high-permittivity (high-κ) dielectric, the requirement of large area to implement high-capacitance capacitors is relieved. The booming field of high-κ dielectric development has ushered in a new era for high-performance MIM capacitors. Among various kinds of high-κ dielectrics, TiO_2 has long attracted great attention because its κ value can be as high as 90~170 when it crystallizes in rutile phase, depending on the lattice orientation. Even with the potential to achieve a high κ value, one inherent material property that limits TiO_2 from further application in MIM capacitors is its high electron affinity which consequently results in high leakage current. Therefore high-work function electrode is always employed for TiO_2-based MIM capacitors to suppress leakage current. In addition, many efforts have been made on doping of TiO_2 with specific metal element to improve its leakage performance such as TiO_2-LaAlO [1], TiTaO [2], TiNiO [3], TiHfO [4], TiZrO [5], and TiPrO [6]. Although doped TiO_2 demonstrates promising results, maintaining the dopant uniformity requires rigorous process control. In fact, reduced leakage can also be obtained by stacking another dielectric with larger band gap such as SiO_2/TiO_2 stack [7]. However, the capacitance density will be inevitably compromised because a larger band gap dielectric usually accompanies a lower κ value. Different from prior arts, in this work, significantly improved leakage current performance for TiO_2-based MIM capacitors can be accomplished by introducing Ge nanocrystals (NCs) into TiO_2. Embedding NCs in dielectrics have been widely adopted in the technology of charge trap flash memory because additional trapping sites can be provided to store injected electrons. Nevertheless the function of charge storage is not required for MIM capacitors, the main reason to introduce NCs is to induce the so-called Coulomb blockade effect or build an internal field to compensate the applied external one, and therefore reduced leakage current can be expected. The results in this work prove the idea by demonstrating a relatively high capacitance density of 25.2 fF/μm^2 with leakage current of 4.6×10^{-7} A/cm^2 at -1 V, which is lower than capacitors without incorporating Ge NCs by a factor of ~1000. In addition, the Ge NCs embedded MIM capacitors show a small loss tangent of 0.020, a low temperature coefficient of capacitance (TCC) of 88 ppm/^{o}C. These promising electrical characteristics attest to the eligibility of the novel structure for MIM applications.

II. Experiment

50-nm Pd was deposited on SiO_2/Si as the bottom electrode of MIM capacitors. Then 29-nm TiO_2 film was deposited as the dielectric of capacitors (denoted as TiO_2 sample). Subsequently, rapid thermal annealing (RTA) of 500 ^{o}C was performed to crystallize TiO_2. To explore the impact of Ge NCs incorporation on electrical characteristics, aforementioned 29-nm TiO_2 was replaced with TiO_2/Ge/TiO_2 laminate structure of 12.5/1.5/12.5 nm for some samples (denoted as TiO_2-Ge sample). With the same RTA condition, Ge NCs embedded in the crystalline TiO_2 is also formed. Next, nitrogen plasma treatment (NPT) was performed on some samples to investigate how nitrogen radicals affect device performance. Finally 50-nm Pd was formed as the top electrode. Brief process flow and device structure are shown in **Fig. 1**.

III. Results and Discussion

Fig. 2 shows the capacitance-voltage (C-V) curves for different process conditions. At 0 V, TiO_2 samples display the highest capacitance density of 33.8 fF/μm^2 while the value for TiO_2-NPT and TiO_2-Ge-NPT samples decrease to 30.2 fF/μm^2 and 25.2 fF/μm^2 respectively. Apparently, NPT process significantly mitigates the dependence of capacitance on applied voltage which makes the capacitors more feasible in circuit applications. As shown in **Fig. 3**, the κ value of TiO_2 is 110.8 which implies the formation of crystalline dielectric after RTA. With NPT treatment, the κ value slightly decreases to 99.0 which is due to the formation of TiON [7]. With additional incorporation of Ge NCs, the κ value further drops to 75.5 because Ge has a much smaller κ value than TiO_2. Although additional plasma treatment or incorporation of Ge NCs results in capacitance degradation, it gains much improved leakage current performance as evidenced in **Fig. 4**. Because nitrogen radials well passivate grain-boundary-related defects in the crystalline TiO_2 film, at bias voltage of -1 V, TiO_2-NPT samples demonstrates reduced leakage current by a factor of 3125 as compared to TiO_2-samples. For TiO_2-Ge-NPT samples, the leakage current further reduces to 4.6×10^{-7} A/cm^2 at -1 V, nearly 3 orders lower than TiO_2-NPT samples. Note that from separate experiments, among these 3 process conditions, TiO_2-Ge-NPT samples enjoy the lowest leakage current under the same capacitance density (not shown). The mechanism of NCs induced leakage current improvement can be understood by the band diagram shown in **Fig. 5**. Due to the conduction band offset of 0.33 eV between Ge NCs and rutile TiO_2 [8], part of the injected electrons from the electrode would be trapped in the Ge NCs. Once NCs are filled with electrons, it may prevent subsequent electrons from further injection by Coulomb blockade effect or build an internal electric field that suppresses subsequent electron injection by compensating the external electric field, and therefore reduced leakage current is expected. **Fig. 6** shows the dependence of normalized capacitance on measurement temperature. For samples with NPT, Ge incorporation indeed helps improve TCC from 113 to 88 ppm/^{o}C. The phenomenon can be explained by the reduced electron injection which causes higher relaxation time and consequently leads to a smaller capacitance variation. Besides the requirement of low leakage current and small TCC, low dielectric loss is also a prerequisite for passive element applications. Dielectric loss quantifies the inherent electrical energy dissipation of a dielectric and the results are shown in **Fig. 7**. At 1 MHz, loss tangent for TiO_2-NPT samples is about 0.045 and the value becomes 0.020 for TiO_2-Ge-NPT samples, which is improved by a factor of 2.2. Since loss tangent is dependent on conductance of the dielectric, once the leakage current can be reduced, improved loss tangent is expected as TiO_2-Ge-NPT samples. **Table I** summarizes the major device parameters for TiO_2-based [3, 4, 7, 9] and other recent [10] MIM capacitors with various electrodes. It is confirmed that plasma treatment of Ge NCs-embedded TiO_2 provides another promising avenue to obtain high capacitance density with much improved leakage current.

IV. Conclusion

Nitrogen plasma treatment was proven as an efficient approach to reduce leakage current of crystalline TiO_2 because of passivation of grain boundary related defects. Further improved leakage performance can be achieved by incorporating Ge NCs into TiO_2. MIM capacitors formed by integrating these processes hold the great potential for future applications in terms of high capacitance density of 25.2 fF/μm^2 with a large value of 75.5, low leakage current of 4.6×10^{-7} A/cm^2 at -1 V, small TCC of 88 ppm/^{o}C and desirable loss tangent of 0.020.

Acknowledgement

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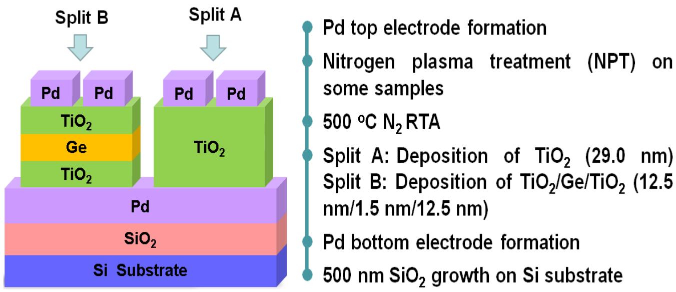

Fig. 1 Process flow of TiO_2-based MIM capacitors. The device structure is not to scale.

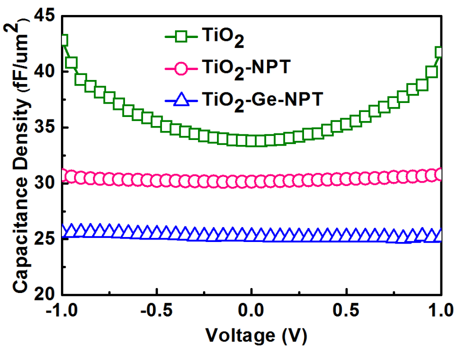

Fig. 2 C-V characteristics for different TiO_2-based dielectrics measured at 1 MHz. Significant dependence of capacitance on voltage can be alleviated by plasma treatment.

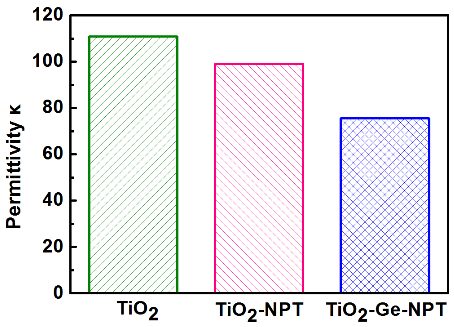

Fig. 3 κ value for different TiO_2-based dielectrics extracted from zero-biased capacitance. The κ value higher than 100 for TiO_2 suggests the crystalline structure.

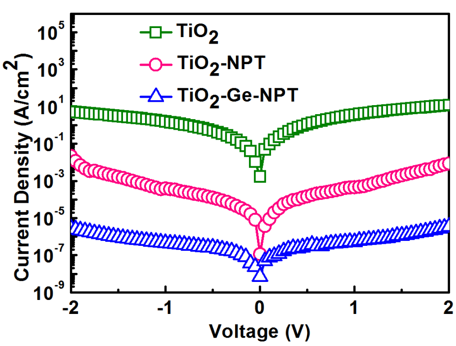

Fig. 4 I-V characteristics for different TiO_2-based dielectrics at room temperature. TiO_2-Ge-NPT shows the lowest leakage under the same capacitance (not shown).

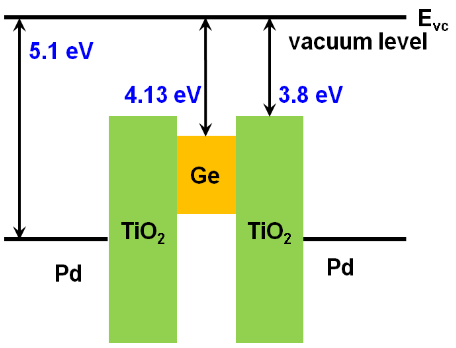

Fig. 5 Band diagram (not to scale) for TiO_2/Ge/TiO_2 MIM capacitors with Pd as electrodes.

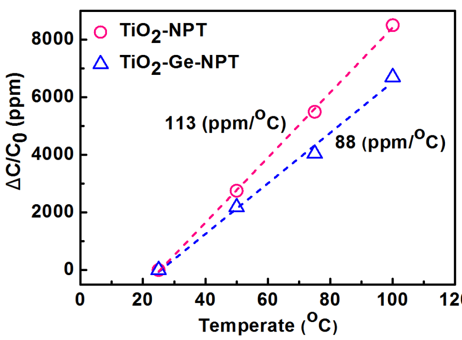

Fig. 6 Temperature-dependent normalized capacitance for TiO_2 dielectric with and without Ge NCs incorporation.

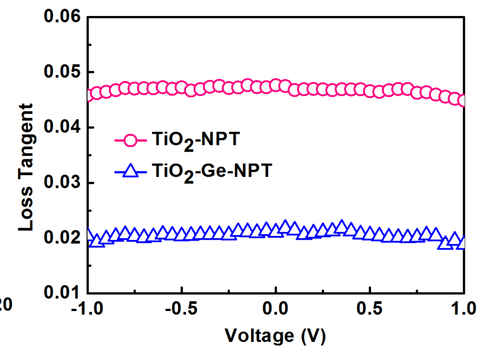

Fig. 7 Loss tangent for TiO_2 dielectric with and without Ge NCs incorporation measured at 1 MHz.

Table I Comparison of major device parameters of TiO_2-based and other recent MIM capacitors with various electrodes.

Material	TiNiO [3]	TiHfO [4]	TiO_2/SiO_2 [7]	TiO_2 [9]	Gd_2O_3/Eu_2O_3 [10]	TiO_2/Ge/TiO_2 This work
Thickness (nm)	20	12	14/2.5	25	8/8	12.5/1.5/12.5
Top/Bottom Electrode	Ni/TaN	TaN/TaN	Al/TaN	Ni_2Si/Ni_2Si	Pt/Pt	Pd/Pd
Work function (eV)	5.1/4.6	4.6/4.6	4.3/4.6	4.8/4.8	5.6/5.6	5.1/5.1
Capacitance Density (fF/μm^2)	17.1	28	11.9	17	12.5	25.2
Current Density at -1 V (A/cm^2)	7.7×10^{-6}	4.8×10^{-6}	8.3×10^{-7}	6.4×10^{-6}	1.2×10^{-5}	4.6×10^{-7}

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