# Effect of $O_2$ Plasma Treatment on the Leakage Current of Titanium Oxide Thin Films Formed via PMODTM

**Isaac Finger, Chemical Engineering, University of Florida**

NNIN REU Site: Microelectronics Research Center, Georgia Institute of Technology
Principal Investigator: Clifford Henderson, Chemical & Biomolecular Engineering, Georgia Institute of Technology
Mentor: Ashwini Sinha, Chemical & Biomolecular Engineering, Georgia Institute of Technology
Contact: ickfin@ufl.edu, cliff.henderson@che.gatech.edu, ashwini.sinha@chbe.gatech.edu

## Abstract:

Photochemical Metal Organic Deposition or PMODTM is a recently reported method for the formation of metal oxide thin films. The present work describes a preliminary investigation into the effect of $O_2$ plasma annealing on the leakage current of titanium oxide thin films formed by the afore mentioned method.

Titanium oxide films resulting from PMODTM were treated with $O_2$ plasma. The treated films were incorporated into parallel plate test capacitors which were then used to measure the leakage current of the dielectric material.

## Introduction:

Due to their characteristic high dielectric constant (k), metal oxides with perovskite structure have been utilized in many current microelectronics technologies. Examples of such technologies are high-density dynamic random access memory (DRAM), microwave tuning devices, and embedded capacitors for electronic packaging. Recent development of procedures for the deposition of these materials as thin films has made such technologies feasible [1-5]. Some applications, such as those using polymeric substrates, require these films to be deposited at low temperature and produced at low cost.

Photochemical metal-organic deposition was first investigated by Hill, et al. [6, 7]. More recently Henderson, et al. have investigated the application of this process for photo-patterning as well as hydrothermal treatment of the products [8]. These studies have yielded a methodology for low temperature, cost effective photo-patternable deposition of titanium oxide and its conversion to the perovskite structure. Investigations into the optimization of each step as well as addition of other treatments to the processing scheme are being carried out to look into the full potential and flexibility of this methodology.

Titanium oxide PMOD forms an amorphous, nanoporous material which can be further processed to direct changes in its structural configuration and electrical properties. This work describes a preliminary investigation into the effect of plasma annealing on the leakage current of these thin films.

## Procedure:

**Spin-Coating and Photo-Conversion:** The PMOD precursor formulation was spin coated on an appropriate substrate using a CEE 100CB spin coater [8]. The coated substrate was then irradiated for 30 min using an OAI Model 500 DUV contact aligner.

**Thermal Annealing:** The photoconverted films were annealed on a hot plate in air at 300°C for 15 min.

**$O_2$ Plasma Annealing:** Samples of the annealed film were treated with $O_2$ plasma in a Plasma-Therm RIE. Treatments were carried out at 30°C, 200 mTorr and 400 W. Treatment times were varied from 5 to 35 min.

**Leakage Current Measurements:** The leakage currents of the plasma treated samples were determined by applying a voltage across parallel plate capacitor structures and measuring the resultant current. MIM (metal-insulator-metal) capacitors were fabricated by depositing a blanket film of PMOD metal oxide on a sputtered platinum coated silicon wafer and depositing sputtered gold top electrodes.

The top electrodes were circles of different sizes (100 μm to 500 μm in diameter). Test probes were contacted to two adjacent top electrodes forming a circuit of two MIM capacitors in series. Current was measured from 0 to 30 V at 100 mV increments using an HP-4156 Precision Semiconductor Parameter Analyzer.

## Results and Discussion:

**Data Normalization:** The circuits tested were effectively made up of a voltage source connected to two identical capacitors in series. Consequently, the data collected from the experiment was normalized to reflect the behavior of one of the capacitors in the series. The current is uniform throughout the circuit and does not need any manipulation. The voltage applied across two capacitors in series is twice that applied to either of them individually. Thus, the data is normalized by dividing the applied voltage of the circuit by 2. The data shown in Figure 1 reflects this normalization.

The leakage current of a capacitor at any applied voltage is directly proportional to the surface area of the capacitor electrode. To compare the leakage currents of different samples the surface area of the capacitors compared was held constant. All data shown herein was collected from capacitors with diameter 300 μm.

The leakage currents of the capacitors tested the experimental increase as a function of the applied voltage. At low voltages the resulting current seems linear and remains close to zero. At some critical point, the current begins increasing rapidly and behaves more like a parabolic or exponential function of applied voltage. Such behavior is an indication that the capacitor is nearing failure. In this investigation, it was found that the voltage where the critical point occurred, in a particular sample, was related to the time of exposure to $O_2$ plasma. From Figure 1 we see that this critical point occurs at a different voltage for each corresponding treatment time.

The critical point for the samples treated for 5 and 35 minutes occur at lower voltages than that of the sample treated for 15 minutes. This suggests that there is a treatment time between 5 and 35 minutes that would correspond to a maximum critical point voltage.

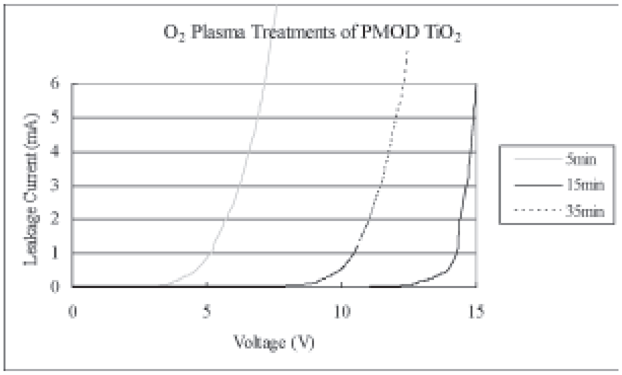

*Figure 1: Leakage Current vs. Applied Voltage of PMOD $TiO_2$ samples treated with $O_2$ Plasma. Treatment times included are 5, 15 and 35 min.*

## Future Work:

We do not have a very good understanding of how the $O_2$ plasma treatment physically changes the titanium oxide film in this procedure. Research to further elucidate the dynamics behind this relationship, as well as find the optimal processing parameters, is currently under way. A better understanding of this treatment will aid in its integration in a larger processing scheme.

## Acknowledgements:

The authors would like to acknowledge the staff of the Microelectronics Research Center at the Georgia Institute of Technology for their attentiveness and technical support.

## References:

[1] J. Scott, Annual Rev of Mats Science 28, 79 (1998).
[2] R. Wallace & G. Wilk, MRS Bulletin 27(3), 192 (2002).
[3] J.Prymak, S.Bhattacharya and K.Paik, in Fundamentals of Microsystems Packaging, R. Tummala, Editor, p. 420, McGraw Hill, New York (2001).
[4] P. Wise, I. Reaney and W.E. Lee, J. Mater. Res. 17(8), 2033 (2002).
[5] R.Ulrich, D. Nelms, L.Schaper and D. Parkerson, High Density Interconnects 1(4), 40 (1998).
[6] R. Hill, et al., Materials Chemistry and Physics 43, 233 (1996).
[7] S. Goetting, B. Palmer, M. Gao and R. Hill, J. Mater. Sci. 29, 6147 (1994).
[8] S.Mukherjee, et al., Electrochem. Soc. 28, 263-275 (2003).