Work Function Of Refractory Metals And Nitrides from CV Analysis

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Abstract – **The work function of p-type and n-type metal electrode materials deposited by RF magnetron sputtering in argon was determined by CV measurements on MOS capacitors. In addition, the work function of p-type and n-type nitride electrode materials deposited by rf magnetron sputtering in nitrogen was also determined by CV measurements on MOS capacitors. The metals deposited were molybdenum, tantalum, titanium, and aluminum. The nitrides deposited contained the metals listed previously with the exception of aluminum. The work functions were determined tó be 4.70 +/- 0.49 eV for Al, 4.46 +/- 0.26 eV for Mo, and 4.22 eV for Ta. Capacitors of the other films are still in the progress for fabrication or require further testing. The work function results of these materials will be published later.**

I. INTRODUCTION

The work function of a material can influence how a device functions as well as the fabrication of the device. Some applications or examples are as follows. The work function of gate electrode material affects V_T of MOSFETs. Also, the metal work function determines the nature of metal-semiconductor contact. In addition, the work function of a material influences field emission.

However, work functions of these materials may not be known or a may contain a high degree of uncertainty in known values. CV analysis can be used to accurately determine work function.

The reference work functions used to compare experimental results were 4.3 for Al, 4.7 for Mo, and 4.3 for Ta.[2] These values may not be the most accurate or most recent but all three were taken from the same source to provide consistency.

II. EXPERIMENTAL PROCEDURES

Capacitors were fabricated on 100mm n-type and p-type wafers with a crystal orientation of <100> and a substrate resistivity between 5-10Ω-cm.

The n-type wafers were doped N+ with spin-on dopant and a predep of 1000C for 30min performed to prevent the formation of Schottky diodes on the backside.

A standard RCA clean was implemented to remove contaminants from the wafers and furnace boat. A TCA clean was also implemented to clean the furnace tube and the boat as well. Oxide growth was performed in dry O_2 at 950C for 32min to grow a 200A oxide. The parameters for the 600A oxide were 1050C for 40 min. Finally, the wafers were pulled at 700C in N_2 to reduce any oxidation from the clean room ambient.

The electrode films were deposited using the CVC 601 and Perkin-Elmer 2400 magnetron sputter systems. The pressure was approximately 1E10^{-6} Torr. Metallic films were sputtered in argon and the respective nitrides sputtered in nitrogen ambients.

P-type and N-type wafers

200A	200A	600A	600A
Al		Al	
Mo	MoN	Mo	MoN
Ta	TaN	Ta	TaN
Ti	TiN	Ti	TiN

Figure 1: Deposited Films

The wafers were coated and developed on a GCA wafertrac. The wafer exposures were completed on a GCA g-line stepper.

The Al and MoN wafers were patterned using an Al etchant (phosphoric acid) for about 2min. The Ta wafers were patterned using RIE etching. The etch parameters were 75W, 125 mTorr, and 30 sccm SF_6 for approximately 2min. The remaining resist was stripped using acetone or an RIE ash.

The backsides of the wafers were deposited with 500A of Al. Next, the wafers were sintered at 450C for 30 min. in H_2/N_2 to improve contacts.

100k um^2 capacitors were tested using equipment that consisted of a PC, Keithly CV analyzers, and the necessary software for the equipment to interact and perform the necessary calculations and measurements. The wafers were measured in a sealed probe box where the chuck was grounded and the probe applied the voltage.

III. RESULTS AND DISCUSSIONS

Calculations were done to obtain the DeBye length, the silicon flat-band capacitance, and ultimately the flat-band capacitance(C_{FB}).
With the C_{FB}, the flat-band voltage(V_{FB}) could be extrapolated from a CV plot or Figure 2.

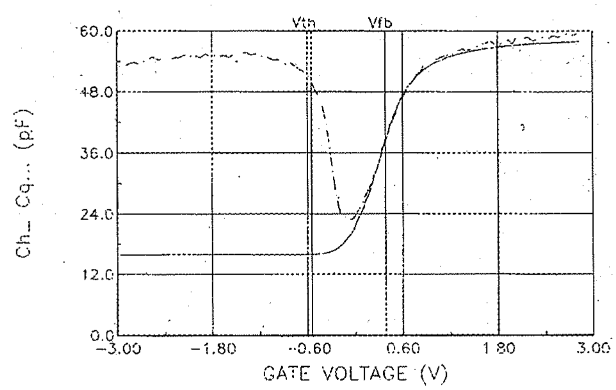

Figure 2: CV Plot of a Mo 600A n-type capacitor

The High Frequency (1MHz) CV plots were obtained using voltage sweeps ranging from –3.0 to 3.0V for 600A n-type capacitors (3.0 to –3.0V for 600A p-type) and –5.0 to 5.0V for 200A n-type capacitors (5.0V to –5.0V for 200A p-type capacitors).

ϕ_{MS} was calculated by the following equation [1]

$$V_{FB} = \phi_{MS} - (Q_F * d_{OX})/\varepsilon_{OX}$$

where V_{FB} is the flat band voltage, ϕ_{MS} is the work function difference between the electrode and substrate, Q_F the fixed charge, d_{OX} the oxide thickness, and ε_{OX} the dielectric constant of oxide

ϕ_{MS} was set equal to V_{FB} under the assumption that the Q_F term was the same for all concurrent wafer processes. Since the 200A and 600A wafers were processed at the same time, Q_F should be a constant for each oxide thickness. As a result, the omittance of this term should introduce minor or negligible error in the final results.

Next, the work function of the electrode(ϕ_M) is obtained by adding the substrate work function(ϕ_S) to ϕ_{MS}. The averaged work function results and the percent error results of each capacitor tested are shown in Figures 3 and 4 respectively.

Metal	Ave. Exp. ϕ_M (eV)	Published ϕ_M (eV) [2]
Al	4.70 +/- 0.49	4.3
Mo	4.46 +/- 0.26	4.7
Ta	4.22	4.3

Figure 3 – Work Function Results

Wafer	Mo	% Error	Ta	% Error	Al	% Error
P-200A	α 1a	**9.83**	δ 3a	**1.90**	α 7a	**12.20**
P-200A	α 1b	**9.63**			α 7b	**13.13**
P-200A	β 1a	**0.12**			β 7a	**20.59**
P-200A	β 1b	**0.96**			β 7b	**19.35**
N-200A	χ 1a	**7.88**			χ 7a	**1.04**
N-200A	χ 1b	**6.76**			χ 7b	**1.94**
N-600A	δ 1a	**4.56**			δ 7a	**6.87**
N-600A	δ 1b	**4.36**			δ 7b	**5.46**

Figure 4 – Percent Deviation from Published Work Function Values

Variations in the work functions could be attributed to a variety of reasons. First, the assumption that the Q_F term is constant and therefore negligible is false. Other defects in the oxide caused by RIE etching of resist for some wafers, and the RIE patterning of electrode materials, could have induced charges into the oxide or degraded in the oxide in some other manner. As a result, the equation

$$V_{FB} = \phi_{MS} - (Q_F * d_{OX})/\varepsilon_{OX}$$

may have neglected a term.

Another source of error could again be do to etching. The capacitors may have been over-etched meaning that their actual area is smaller compared to the area of the same capacitor on the reticule. Therefore, measurements understate theoretical values used for calculations.

Also, the electrode films sputtered may not have been thick enough. Approximately 2000A should have been sputtered and some of the films were less than 800A. As a result, these films could have been punctured by the contact probe, and therefore, would give false capacitance measurements by understating them if or if results could be obtained at all.

IV. CONCLUSIONS

The work function results were found to be relatively accurate. By limiting RIE etching to essential steps, and in turn optimizing the endpoints of these etches, better testing results should be obtained. Also, better observation of film deposition and measurement should also be incorporated into the process. In addition, the use of a non-contact probe could alleviate some of the high serial resistance problems during CV analysis.

Additional work would be to complete the fabrication of capacitors using the electrode metals and nitrides listed in Figure 1. Also, future work could include the addition of other films such as NbN or Pt. Finally, extensive and more comprehensive testing is required to obtain accurate results.

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REFERENCES

[1] P.E. Hellberg, S.L. Zhang, and C.S. Peterson. "Work Function of Boron-Doped Polycrystalline Si_XGe_{1-X} Films." *IEEE Electron Device Letters*. Vol. 18, NO. 9, September 1997 p.456-458

[2] Literature Dr. Turkman has on Work Function Chart