Work Function Engineering With Molybdenum and Molybdenum-Nitride Gate PMOS

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Abstract – The motivation for the creation of RIT metal gate PMOS process transistors was to investigate and prove the work function of molybdenum can be changed through reactive sputtering and thermal processing. The existing RIT metal gate PMOS process was adapted to form Molybdenum and Molybdenum-Nitride PMOS transistors. Processing of the molybdenum films affected the final composition of the gate electrode and ultimately its work function. Through theoretical and real analysis, the work functions of Mo and MoN gates were extracted and compared with one another as well as to Al. Examination of the extracted work functions revealed the presence of other phenomena accountable for 1.5-2.0V shift in Vt from one gate type to another. While no single mechanism is identified as the source of extra charge, contamination of the Mo/SiO2 interface, oxidation of the Mo, work function difference, or some combination of all three are likely to explain the shifts in threshold voltages.

Index Terms – Work function, PMOS, Amorphization

I. INTRODUCTION

The 2003 International Technology Roadmap for Semiconductors predicts that by 2005-2007, the CMOS industry will steer toward several paradigm shifts in standard processing to meet the projections of Moore’s Law. Specifically it is projected that the polysilicon gate electrode and SiO2 gate dielectric will be replaced with alternate materials. A major goal of replacement gate technology is the ability to tune the threshold voltage via the gate metal work function independently for PMOS and NMOS transistors. With a focus on reducing gate resistance and preventing tunneling and leakage current, a modification of the currently used RIT Metal Gate P-type MOS process has been created. The modification concentrates on the replacement of the Aluminum gate with the mid-gap work function metal of Molybdenum and Moly-nitride. Research shows Mo and MoN to be compatible with other dielectric films. Because so much attention is given in research to hi-k dielectrics, it is important to recognize that alternative gate materials must be well suited for them. The Mo work function of ~ 4.5eV makes it a promising candidate material for use with Silicon substrates. Because it is a metal, it ensures the prevention of gate depletion and offers significant reduction in resistance. However, in using metal gate materials, the work function required for a desired threshold voltage is not so easily achieved or changed and either must be varied with an alloy mixture and/or dimension. By conducting this project, the establishment of an alternative gate process at the RIT SMFL will be achieved. Additional knowledge of the benefits and drawbacks of alternative gate materials will be realized.

II. MOTIVATION

As scaling of integrated circuits continues, new challenges for engineers arise. As channel lengths become smaller, the issues with polysilicon as gate electrode tends to grow. Resistance at the gate becomes an issue, as this characteristic does not scale equally with channel length. Also, with existing CMOS technology threshold adjustment doping at the gates can be hard to control. If the gate material is doped to heavily, excessive concentrations of dopant in the gate can punch through thin gate oxides (assuming SiO2). If doped too lightly, depletion of dopant from the gate/dielectric interface may occur. This gives rise to the poly depletion effect.

Manuscript received May 19, 2004. This work was supported in part by the Rochester Institute of Technology, Department of Microelectronic Engineering. V. Welsh is with the Rochester Institute of Technology, Rochester, NY 14623 USA (e-mail: vcd6212@rit.edu).
mechanism is responsible for degradation of drive current and increases the effective oxide thickness.

III. DEVELOPMENT

Using Molybdenum as the gate electrode would resolve these issues. As a highly conductive metal, Mo offers low gate resistance. Its thermally resilient melting temperature of 2610°C and thermal coefficient of expansion of 5E-6/°C 20°C allow for much greater latitude with thermal budget and alleviates concerns regarding interfacial lattice stress. These characteristics make Mo attractive for self-aligned gate technology. Molybdenum also has a stable contact with SiO₂ up to 1000°C again fitting nicely with existing and aging technology. Most importantly however, is the range of work functions this material is reported to have.

According to Ranade, the reported work function values for Molybdenum range from 4.2 to 4.7 electron volts. When implanted or otherwise combined with other materials and processed this range has been seen to vary 4.0-5.0eV[1]. Ranade’s work has shown that post sputter annealing alone (400-900C) will raise the Mo work function by .7 or .8 volts indicating that thermal processing has an effect on Molybdenum films. According to his work, “annealing in argon ambient produced results similar to annealing in forming gas ambient even after taking the effects of oxide fixed charge into account.” This work function has been altered by almost a volt before implanting or reactively sputtering it with anything else. It is generally accepted that the work function for molybdenum in device applications is dependent upon the conditions of its deposition and subsequent processing. Sputtering is the most widely used method for deposition. It is surmised that only plasma is feasibly capable of depositing refractory metal films. While literature is scarce, it is believed that the work function of Mo is initially determined at the initial deposition [2]. The morphology of the film at the dielectric interface is theorized to determine the work function of the film in this area. Naturally then the initial state of the film morphology will ultimately influence the final arrangement of the film and the measured work function.

A high percentage of the research available addresses the implantation of nitrogen and argon into sputtered molybdenum films. The formation of Moly-nitride through implantation is theorized to amorphize the Mo film structure. The breakage of surface bonds is detected by a negative shift in the flatband voltage. The corresponding work function is therefore lowered.

Process
Adapted from RIT’s metal gate PMOS process, one lithography mask was substituted and one added to incorporate Aluminum contacts and Molybdenum and Molybdenum-nitride gate electrodes. The metal gate PMOS process:

- Scribe, 4pt probe, RCA Clean
- Masking Oxide Growth 5000Å

Figure 2: Representative Cross-section through pattern oxide growth
- Level 1 Lithography opens S/D regions
- Pattern Oxide through BOE

Figure 3: Representative Cross-section through S/D opening
- RCA Clean, Spin on Boron Dopant
- Furnace Pre-deposition
  - drives dopant into surface
  - consumes Si in S/D region

Figure 4: Representative Cross-section through SOG application
- BOE all material from surface

Figure 5: Representative Cross-section through S/D predeposition
- Grow Field Oxide 5000Å while driving in S/D

Figure 6: Representative Cross-section through Field Oxide growth and S/D drive-in
- Level 2 Lithography opens active device area
- Pattern Oxide through BOE

Figure 7: Representative Cross-section through active area definition
IV. FABRICATION

The current PMOS process uses Al for the gate and source/drain contact. Recently Boise State University in conjunction with RIT has conducted research using alternative gate materials and had ordered a lithography mask for this process that patterned the gate separately. The process uses a spin on glass for the source and drain formation followed by a drive in and field oxide growth process that gives a junction depth of about 1.5µm. Aluminum was used for the source and drain to ensure and ohmic contacts in these regions. The aluminum pattern was followed by a lot split where some wafers received Mo sputter deposition and others were reactively sputtered with MoN.

A separate designed experiment with reactive sputtering was conducted to determine what ratio of nitrogen was appropriate in the creation of a Moly-nitride film. As nitrides are classically insulators, the DOE was used to establish what percentage of nitrogen in the sputter would give the lowest resistivity.

At the lower limit of the nitrogen flow, resistivity in the Moly-nitride film dropped from independently sputtered Molybdenum. As the incorporation of nitrogen in the film increased, tensile stress in the film was more and more evident and resistivity appeared to increase linearly. While the experiment was not repeated, the substrates used were of various oxide thicknesses in attempts to normalize the results. The theory is that plasma induced damage would have the same amorphizing effect on the sputtered film as the nitrogen implantation of previous research. A 3% ambient content of Nitrogen was concluded to give the lowest resistance.

Once the gate electrode material was deposited the original RIT metal gate PMOS gate and contact mask was used. This resulted in the formation of a double contact to the source and drain, the wafers were then etched with the same phosphorous wet Al etch chemistry and sintered in forming gas at low temp.

V. RESULTS

Following the sinter process, the appearance of the devices showed corrosion and contamination of the gate material.
Microscopic inspection revealed the gate material was brown “spongy” in appearance and easily removed.

In fact, “MoO2 is known to be conductive and hence as long as the MoO2 is formed without chemical reaction at the interface, oxidation is unlikely to alter the oxide capacitance.” --Ranade[1].

Without an without timely access to (EDS) analysis one cannot definitively say whether Mo or MoO2 is present on the gate.

Further analysis a threshold voltage shift from Al to Mo gate transistors on the same chip. With “documented” work functions of Al=4.1 & Mo=4.5 The calculated difference between the metals should be approximately .4volts. It stands to reason identically manufactured transistors would be expected to exhibit just this shift. Even with a widely ranging work function for the Mo, there remains a 1.5- 2 volt shift in positive direction for Vt. This amount of charge must then be accounted for with Nss & substrate doping. Understanding that almost all incidental are positive in nature, and that those encountered would push the threshold voltage to be more negative there arises the question of where negative charge could have been picked up and trapped after the aluminum deposition.

Notice again the process flow used. With this sequence, the gate oxide cannot be cleaned once the aluminum is applied. Using the aluminum etch followed by an IPA/IPO resist removal process offered the first and best possibility for source contamination. The threshold voltage and flatband equations are typically used to extract the quantity of excess charges in a device when the gate work function is already known. Using the documented value for the Al work function, the excess trap charge density was calculated to be 1.26E19/cm. Using this estimation for the adjacent Molybdenum gate device the work function of the gate electrode was calculated to be 5.99eV.

MoN Re-process Description
Recognizing that only two processes were performed with Molybdenum (pattern and sinter) the remaining wafers were re-processed to determine whether the wet Al etch or the sintering would give rise to this same Vt shift. Both wafers were cleaned, and 1500Å of Al evaporated, patterned and etched with the same Phosphorous Al etch bath. Again the IPA/IPO solvent resist removal was performed. Then one of the remaining two wafers was sintered at 400°C 30min and both reactively sputtered with 1700Å of Molybdenum-nitride (3%). The MoN gates were then patterned and the sintered wafer etched again with the Al wet etch. The other wafer was plasma etched with SF6 for 3min, solvent removal performed again followed by its own sinter.

The wafer that received no MoN thermal process produced a comparable family of curves to the original Mo gate devices, but looked very different.
Indeed, the threshold voltage was lower than that of the Mo gate device as predicted. The wafer that received the plasma MoN etch followed by a sinter in forming gas appeared as expected upon emergence from the furnace. Unexpectedly though, none of the devices tested have yet yielded.

VI. CONCLUSIONS

Regarding the comparison of Mo to MoN gate transistors, the extracted work functions for each were found to be $-0.7$ and $-2.0$ volts respectively. While the work function of the gate materials has shifted 1.3 volts, the Al to Mo gate comparison and the appearance of the Mo post sinter cannot be ignored. The threshold voltage difference is more likely the result of a combination of work function difference, contamination from negative charges in the wet metal etchant, and the nature of the oxidized film at the gate. The last of these hypotheses is supported by the belief that oxidized Molybdenum would raise the work function of the gate electrode.

The first, best solution to guarantee a Mo to MoN gate electrode comparison would be the manufacture of the gate first as is ideal in self-aligned gate processes. Further work should also be done to ensure that the Mo is not oxidized during subsequent processing.

ACKNOWLEDGMENTS

The author acknowledges Dr. L. Fuller for advisement on this project. Dr. K. Hirshmann, Dr. S. Kurinec, and Dr. J. Moon for research guidance. M. Aquilino, R. Vega, and J. Steinfelt for questions, and T. Prevost, B. Curanovic, and J. Cabacungan for support. Also the SMFL staff for direction and tool solutions.

REFERENCES


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