

A Combinatorial Study of Metal Gate/HfO₂ MOSCAPS

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Combinatorial methodology is a rapid technique for surveying new gate dielectrics and gate metal electrodes for the very complex advanced CMOS gate stack. Here, we report on a typical metal gate electrode alloy system, the Ni-Ti-Pt ternary. We have fabricated this metal gate thin film library on HfO₂ using magnetron co-sputtering, to investigate flat-band voltage shift (ΔV_{fb}) and leakage current density (J_L) variations. Wavelength dispersive spectroscopy (WDS) results show that compositions containing up to 90% of Ni and Ti, and 75% of Pt were attained in the library. A more negative ΔV_{fb} is observed close to the Ti-rich corner than close to the Ni- and Pt-rich corners, implying smaller work function (Φ_m) near the Ti-rich corners and higher Φ_m near Ni- and Pt-rich corners. Measured J_L values are consistent with the observed ΔV_{fb} variations.

Introduction

The Si microelectronics community is currently faced with major materials challenges to further scaling. The gate stack that has served the industry for 35 years, i.e., the SiO₂ gate dielectric and degenerately doped polycrystalline Si gate electrode, must now be entirely replaced with one having a higher capacitance and a lower leakage current. High-k gate dielectric substitutes for SiO₂, and metal gate electrode substitutes for polycrystalline Si must be found. The International Technology Roadmap for Semiconductors (ITRS) dictates that a 0.8 nm equivalent oxide thickness (EOT) gate dielectric is required for the 50 nm technology node in 2009 (1). High-k gate dielectrics have been studied extensively, and many potential materials such as HfO₂, ZrO₂ and their silicates and oxynitrides, have shown promise as replacements for SiO₂ (2-4). However, identification of the proper metal gate electrodes is not as advanced.

Metal gate stack integration involves complex electrical issues such as the work function, flat-band voltage shift, and oxide charge, in addition to the thermal stability of the gate stack with regard to crystallization, interdiffusion, and interfacial reactions (3,5). Elemental metal gates, even with appropriate band structure, may suffer adhesion and thermal stability problems (6). Alloy metal gates might be a better solution, since one can tailor the desirable properties. However, exploring metal gate electrode alloys is not trivial, since fabrication based on a one-composition-at-a-time approach is too time consuming, even for just one of the many possible ternary alloy systems. Combinatorial methodology, a high throughput and rapid characterization approach, offers a viable solution, since a large number of samples may be characterized at once (7,8).

The goal of this paper is to demonstrate the efficiency of combinatorial techniques to enable rapid exploration of the electrical and physical properties of a ternary metal gate electrode system on HfO_2 , through the deposition of a combinatorial ternary alloy “library”.

Combinatorial Methodology

Combinatorial methodology is a fast and relatively inexpensive product discovery tool that has revolutionized the pharmaceutical and genomics industries. It is characterized by high throughput parallel experiments, automated analysis and the creation of massive data sets. Combinatorial methodology has rapidly become a new paradigm to accelerate materials research in fields such as thermoelectrics, high- κ gate dielectrics, transparent magnetic films, high T_c superconductors, ferroelectrics, magnetic semiconductors, and catalysts (9).

Application to the Advanced Gate Stack

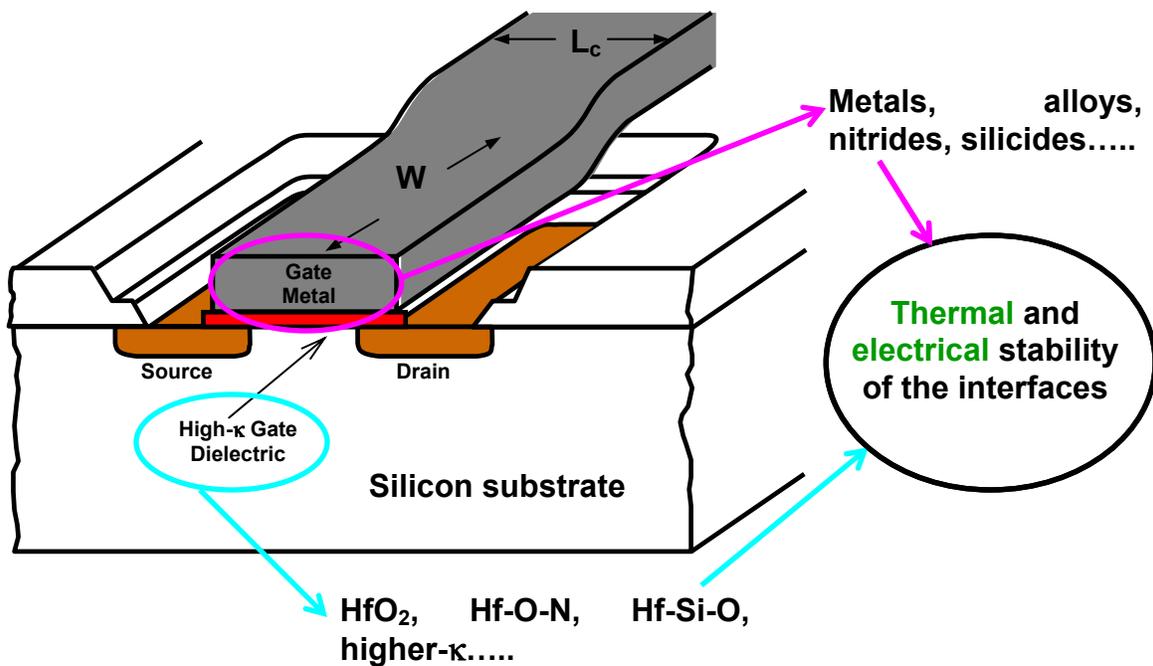


Figure 1. Schematic depiction of a CMOS transistor showing the advanced gate stack.

Figure 1 schematically depicts an advanced MOS device, showing the metal gate electrode and the high- κ gate dielectric. The advanced gate stack is a very complex materials science problem, ideally suited for combinatorial methodology. Although the industry has tentatively settled on HfO_2 -based high- κ gate dielectrics, there are many possible variations, including nitrides and silicides. In addition, as can be seen from Fig. 2, the list of candidate gate metals is very large. There are far too many possible combinations of gate dielectric and gate metal electrode to be investigated by traditional means. Further, in the near future the advanced gate stack will be grown on high mobility channels such as Ge, strained Si, and GaAs, which will make the problem even more complex.

Figure 2 shows the work functions of many common metals, silicides and nitrides. For a CMOS device, two metal gate electrodes, one whose work function (ϕ_m) is aligned with the Si conduction band (for NMOS), and the other whose ϕ_m is aligned with the Si valence band (for PMOS), are required. The work function values shown in Fig. 2 are for bulk materials, and one can see that there is much spread in the data. However, as a guide, one can look at ternary metal systems containing metals suitable for both NMOS and PMOS, combined with a mid-gap metal. The Ni-Ti-Pt ternary alloy system is such an example. One might find a suitable (proper work function, adhesion and thermal stability on the gate dielectric) NMOS metal alloy near the Ti-rich corner, and a PMOS metal alloy near the Pt-rich corner. The addition of Ni at either end will allow one to tailor the work function of the thin film precisely.

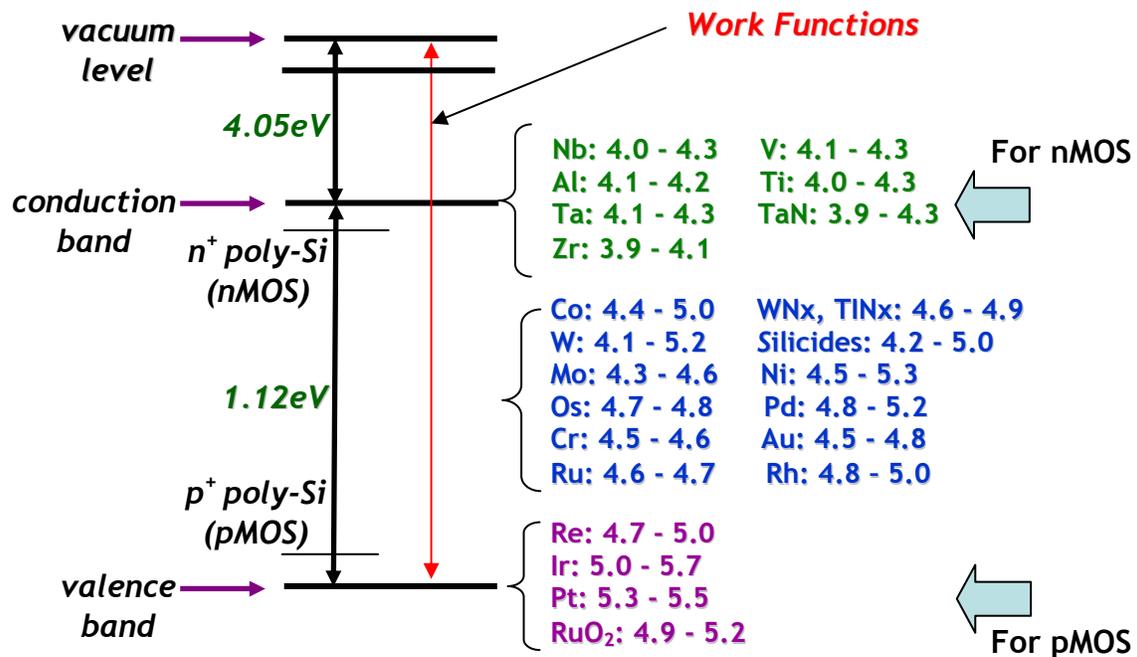


Figure 2. Work functions of various metal gate electrode materials.

Synthesis of Combinatorial Thin Film “Libraries”

One method for preparing the gate metal alloy “libraries” (i.e., a compositionally variable thin metal film in which all alloys are represented) is depicted in Figs. 3-6, for the case of binary alloys. There is a source for each of the two metals (in the illustration a pulsed laser deposited source is used, but it could be evaporation or sputtering as well) that is separated from the substrate by a sliding shutter. With the source on, as the shutter moves from left to right, a wedge of metal A is deposited on the substrate (Fig. 3). The wedge height can be controlled to atomic dimensions by proper control of the source fluence and the shutter travel speed. Rutherford backscattering is used to calibrate the shape of the wedge, so that composition at any point in the binary alloy film is known. Wedge heights of 0.3 – 1.0 nm are typical. In Fig. 4, one can see that the sample can be rotated by 180°, metal source B activated, and the shutter now moved from right to left.

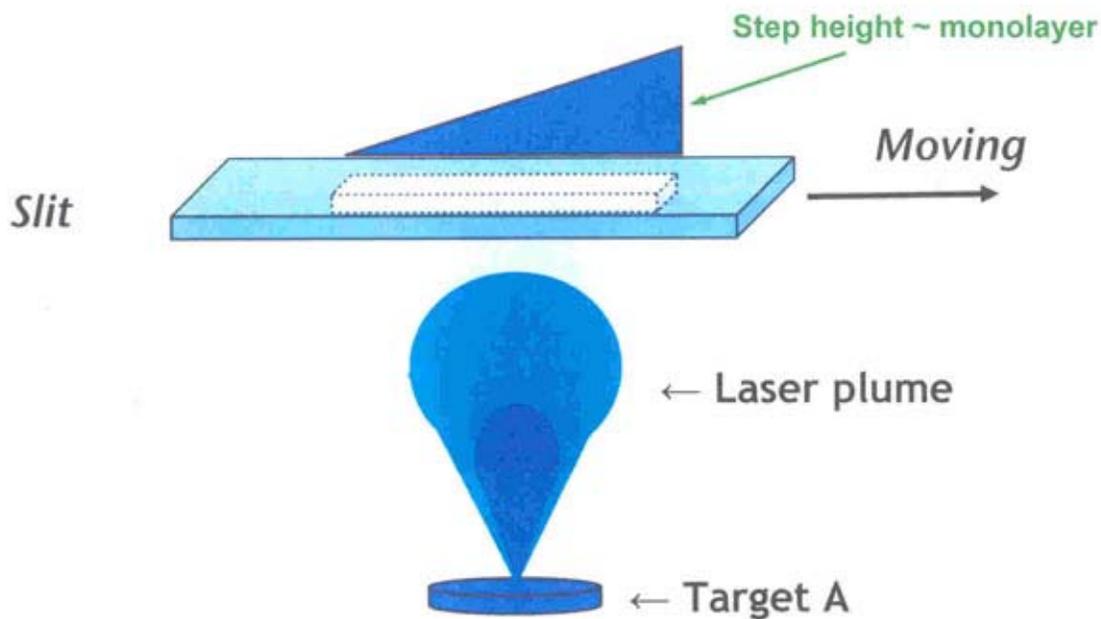


Figure 3. First step in making a combinatorial film library with a composition variation: deposition of a wedge of metal A.

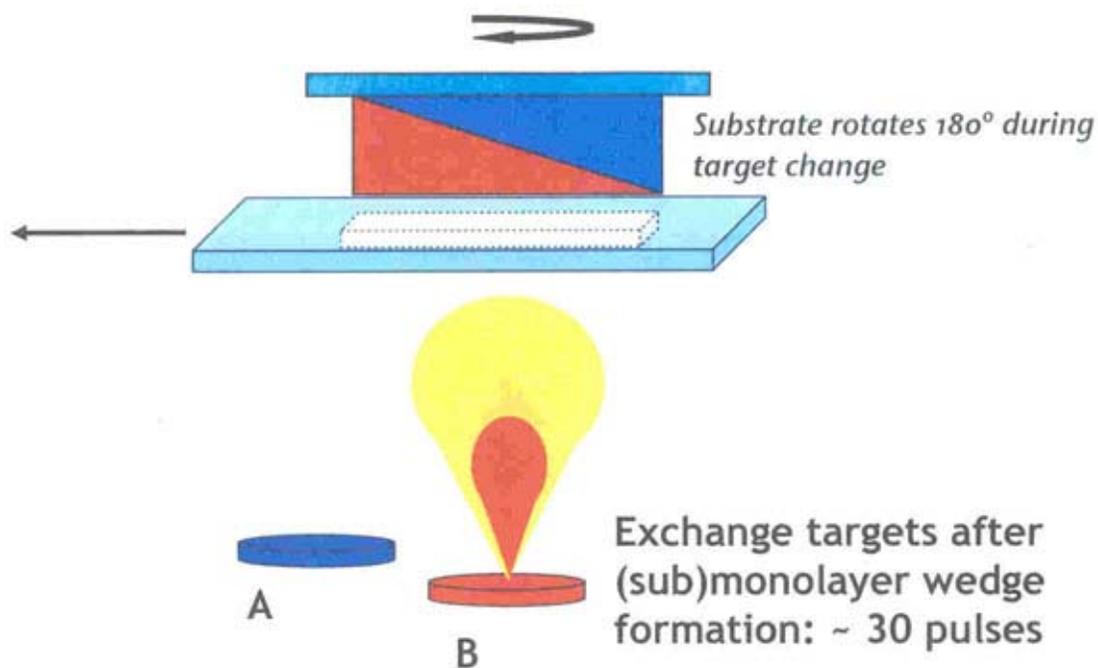


Figure 4. Second step in making a combinatorial film library with a composition variation: deposition of a wedge of metal B.

A complementary wedge of metal B is now deposited on the metal A wedge. Because the wedge height is of atomic dimensions, the two layers are intimately mixed even in the as-grown condition. As in shown in Fig. 5, the binary alloy film may be grown to any thickness, simply by depositing as many A-B wedge pairs as is desired. Since only a few atomic jumps are necessary to homogenize the alloy in the thickness (z) direction, a modest anneal will result in a film that varies from pure A on one end to pure B on the

other. Finally, one can imagine that if the substrate were rotated by 120° instead of 180° , and another source, C, were activated, the complete ternary A-B-C could be deposited. This is shown in Fig. 6, from a top view. On the shoulders of the ternary are the respective binaries, and at the edges the pure metals can be found. The entire ternary library film can occupy an area less than about $(2.5 \text{ cm})^2$.

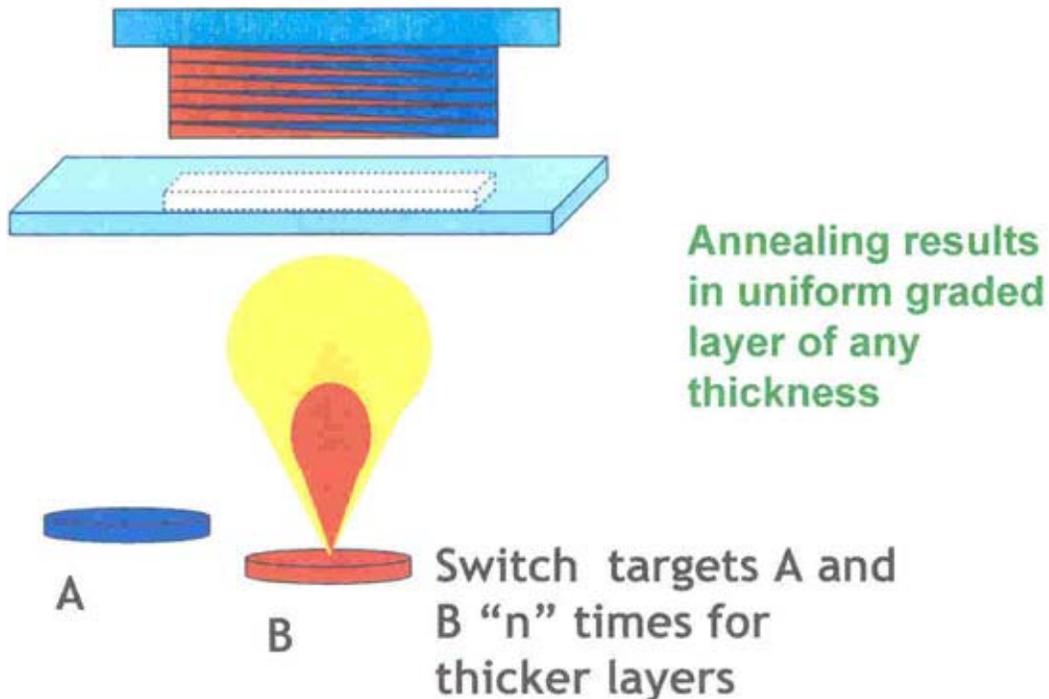


Figure 5. Deposition of a combinatorial film library of any thickness through the use of N layers of wedges A and B. The film composition varies from pure A on the right to pure B on the left.

Electrical and Physical properties of Combinatorial MOSCAPS

One example of a combinatorial library we have fabricated is the Ni-Ti-Pt ternary metal gate electrode system. This system is interesting due to the wide range of work functions represented (Ni: 4.9 eV, Pt: 5.3 eV, and Ti: 4.1 eV) (10), which is good for dual metal gate electrode applications, as discussed earlier. The results shown below are for a library deposited by magnetron co-sputtering, using a "natural" compositional spread method, as opposed to the shutter system described in Figs. 3-6; however, the same combinatorial principles apply. We were able to achieve most of the composition range in this system: up to 90 at. % Ni, 90 at. % Ti, and 75 at. % Pt, as measured by wavelength dispersion spectroscopy. Hundreds of MOSCAPS were fashioned by deposition of the library film through a shadow mask, onto a 6 nm ALD HfO_2 film on a Si (100) wafer. Fig. 7 shows the actual capacitors. It is important to realize that each capacitor depicted has a slightly different composition from the ones next to it.

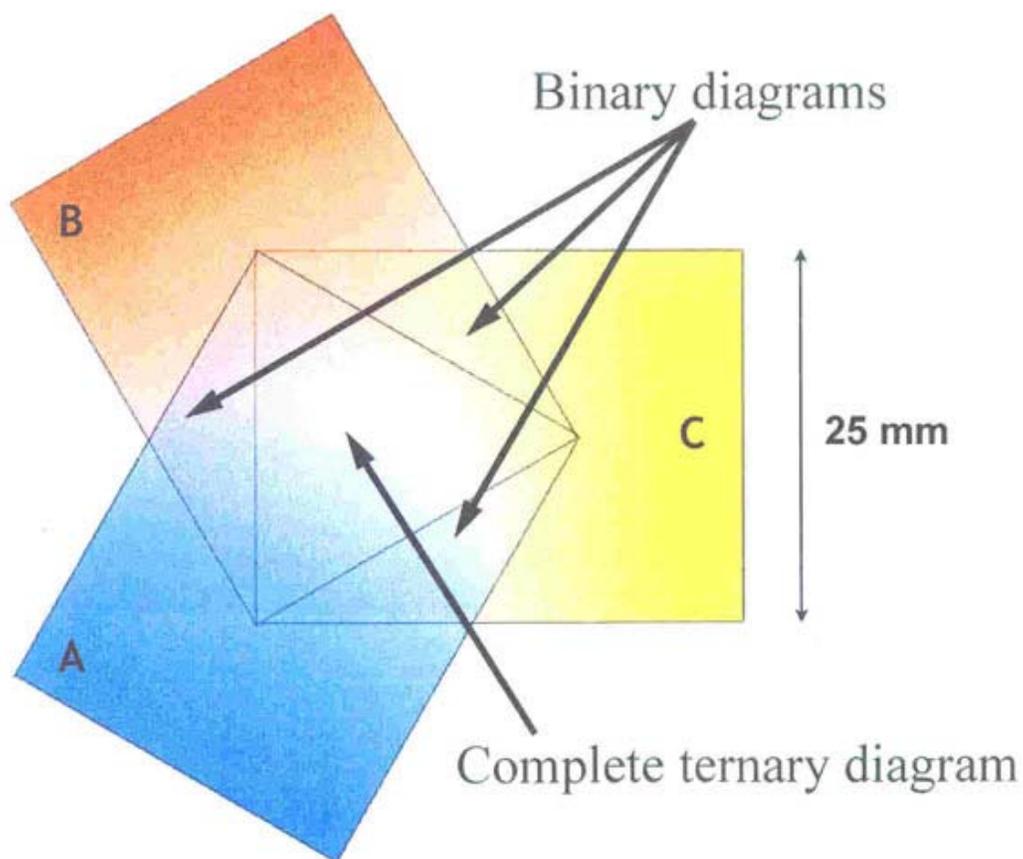


Figure 6. Ternary library film of the system A-B-C.

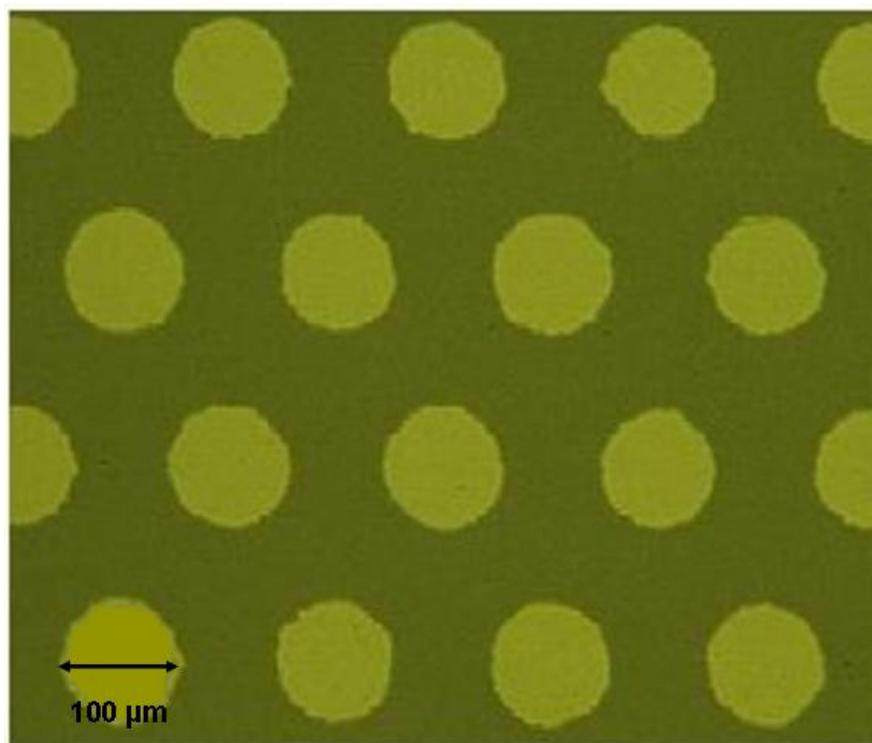


Fig. 7. MOSCAPS in the combinatorial film library.

A forming gas anneal (90% N₂ and 10% H₂) was carried out at 500°C for 30 minutes to lower the interface state density of the as-deposited capacitors. Fig. 8 shows the results of automatic fitting of a typical Capacitance-Voltage (C-V) curve using the Hauser CVC program (11). Flatband voltages (V_{fb}) and leakage currents were extracted from the C-V and Current-Voltage (I-V) curves, respectively. The MOSCAP effective oxide thickness (EOT) values should, to a first approximation, be the same for all metal electrode compositions, since the HfO₂ film is uniformly 6nm thick. We observe an average EOT of about 1.9 nm, greater than the nominal EOT value expected for 6 nm HfO₂ (corresponding to 1.2 nm, assuming a dielectric constant for HfO₂ of 20), due to an interfacial oxide layer between HfO₂ and the Si substrate, which was observed by TEM (not shown).

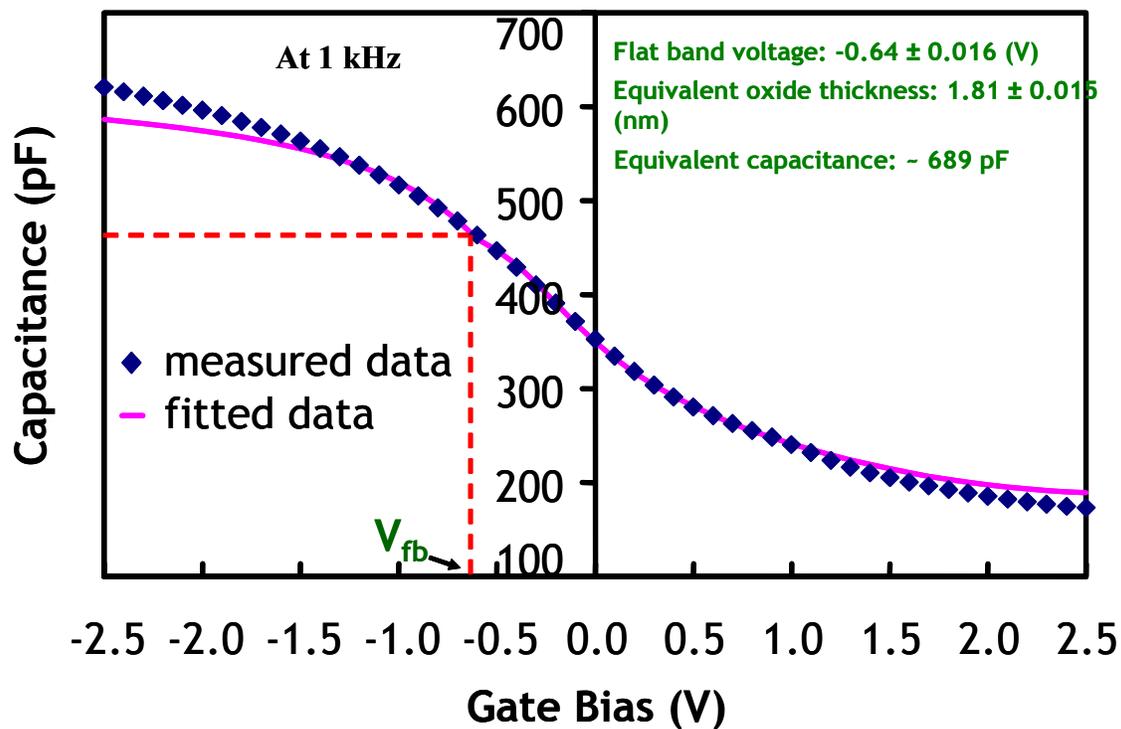


Fig. 8. Automated fitting of C-V data using the Hauser program.

The ΔV_{fb} data are plotted as a function of composition in Fig. 9. A generally systematic and smooth variation is observed across the library. The few black data points represent non-working devices. The smooth variation of ΔV_{fb} suggests that many of the phases present in the bulk Ni-Ti-Pt alloy phase diagram are suppressed in the thin film; clusters of deviant points, such as are seen near the composition Pt₂₅Ti₇₅, may be indicative of an intermetallic compound. V_{fb} and Φ_m are related:

$$\Delta V_{fb} = (\Phi_m - \Phi_s) - (Q/C_{ox}) \quad [1]$$

where Φ_m and Φ_s are the work functions of metal and Si, Q is the charge in HfO₂, and C_{ox} is the capacitance. Assuming Q/C_{ox} is constant during the metal deposition, the variation in ΔV_{fb} is directly related to the change of Φ_m . The ΔV_{fb} values close to the Ni- and Pt-rich corners are less negative (~ -0.3 V) than at the Ti-rich corner (~ -0.8 V). From eq. 1

therefore, Φ_m near the Ni- and Pt-rich corners should be larger than at the Ti-rich corner, consistent with expected values. However, the range of ΔV_{fb} variation within the ternary system ($\sim 0.5V$) observed for the Ni-Ti-Pt library is smaller than expected, based on bulk values. This might be interpreted in two ways: 1) only 75 at. % Pt was achieved, limiting the range of ΔV_{fb} (smaller Φ_m) compared to 100% Pt, and/or 2) mid-gap states were created at the metal/HfO₂ interfaces, resulting in interface dipoles and Fermi-level pinning (12).

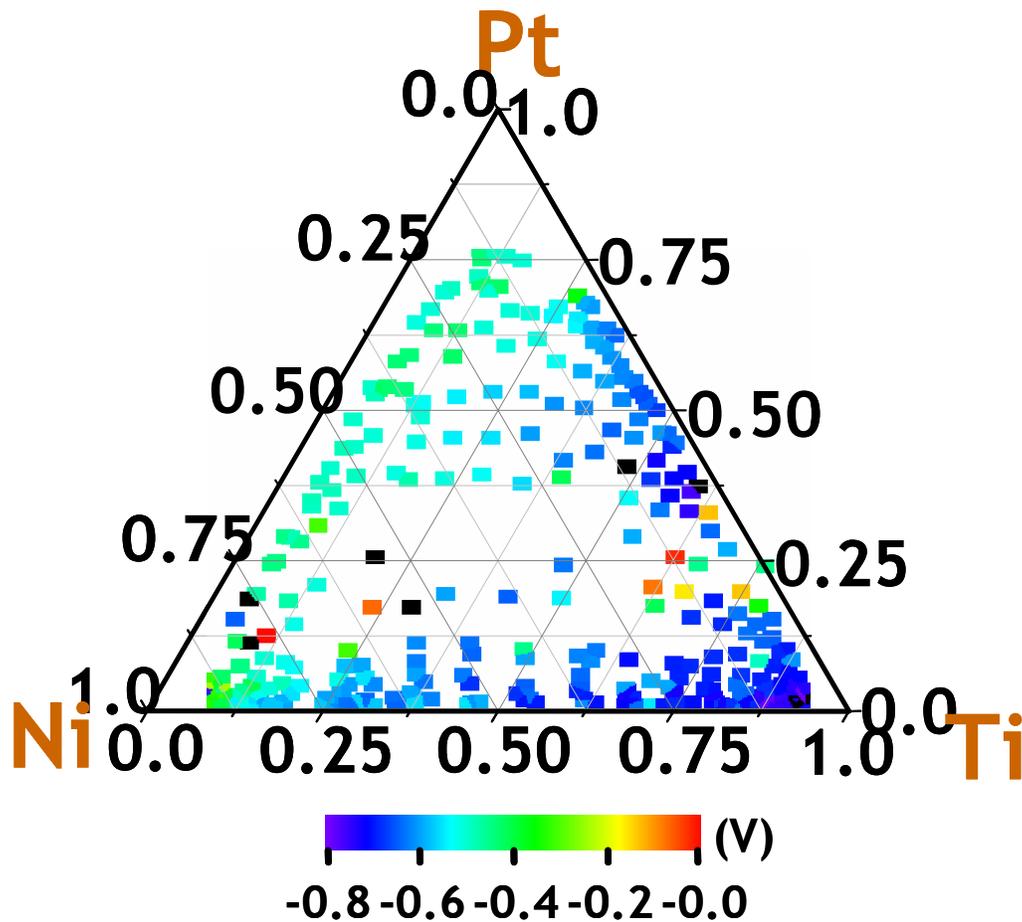


Fig. 9. ΔV_{fb} map extracted from MOSCAPS across the Ni-Ti-Pt library.

Figure 10 shows the leakage current data for the MOSCAPS in the Ni-Ti-Pt/HfO₂ capacitor library. We observe that the devices near the Ni- and Pt-rich corners have smaller J_L ($\log J_L$ (A/cm²) ~ -7.4), gradually increasing towards the Ti-rich corner ($\log J_L \sim -5.9$ A/cm²). These measured J_L values are comparable with literature values (13). From the energy band diagram of metal/insulator/semiconductor structures (14), metals with higher Φ_m intrinsically possess higher barrier heights, based on the equation:

$$\phi_0 = \Phi_m - \chi_i \quad [2]$$

where χ_i is the insulator electron affinity and ϕ_0 is the barrier height. From the data of Fig. 9, Ni- and Pt-rich alloys, possessing higher effective Φ_m , should accordingly have higher

ϕ_0 , and Ti-rich alloys, possessing smaller effective Φ_m , smaller ϕ_0 . The relationship between J_L and barrier height (ϕ_0) is shown in the following equation:

$$J_L \propto E^2 \exp \{(-8\pi/3qhE)(2m^*)^{1/2} (q\phi_0)^{3/2}\} \quad [3]$$

where E is the electric field across the oxide, q is the charge of an electron, h is Planck's constant, and m^* is the effective mass of an electron in the oxide. Higher ϕ_0 results in smaller J_L . Therefore, Ni- and Pt-rich alloys will result in smaller J_L , and Ti-rich alloys higher J_L .

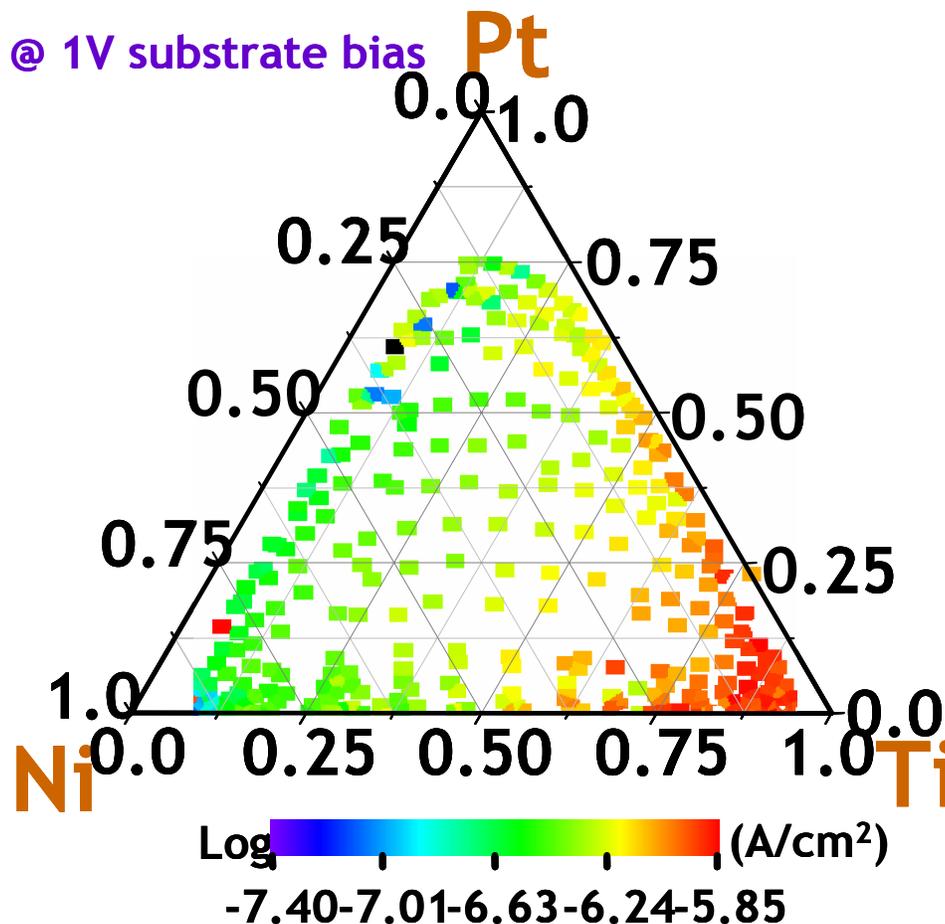


Fig. 10. Leakage current map extracted from MOSCAPS across the Ni-Ti-Pt library.

The metal gates were also studied by x-ray microdiffraction. Whereas polycrystalline structures are observed near the Pt- and Ni-rich corners, there is no indication of Ti peaks near the Ti-rich corner, which implies either an amorphous or nano-crystalline structure for the Ti-rich alloys. The Ni-Ti-Pt system is rich in intermetallic compounds, but they are not observed in our thin film structures. This could be because they are 1) not stable (or kinetically suppressed) in thin film form, or 2) are highly textured or present in small volume fractions and are not seen in the diffraction patterns.

In conclusion, Ni-Ti-Pt ternary metal gate libraries were deposited on HfO₂ dielectrics, and studied systematically by WDS, x-ray microdiffraction, C-V and I-V. WDS results show that over 90% ± 1% of Ni and Ti, and 75% ± 1% of Pt were attained in the library. The polycrystalline structures of Ni and Pt, and amorphous or nanocrystalline structure of Ti, were confirmed using scanning x-ray microdiffraction. The fitted C-V characteristics reveal the mode of the EOT value is about 1.9 nm, larger than expected, due to interfacial oxide. A more negative ΔV_{fb} is observed close to the Ti-rich corner than close to the Ni- and Pt-rich corners, implying smaller Φ_m near the Ti-rich corners and higher Φ_m near Ni- and Pt-rich corners. In addition, measured J_L values are consistent with the observed ΔV_{fb} variations.

Acknowledgments

The authors would like to acknowledge the assistance of J. Suehle and H. Xiong (NIST), J. Hattrick-Simpers and O. Famodu (UMD), K. Ohmori and P. Ahmet (NIMS), and P. Majhi, B.-H. Lee and M. Gardner (Sematech).

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