

Variable Interface Dipoles of Metallated Porphyrin Self-Assembled Monolayers for Metal-Gate Work Function Tuning in Advanced CMOS Technologies

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Abstract—This paper presents a technique for continuous tuning of the metal-gate work function (Φ_{metal}) using self-assembled monolayer (SAM) of metallated porphyrins. Porphyrin SAM was prepared on SiO_2 followed by Al evaporation to form MOS capacitors (MOSCAPs). The variation in the dipole moment achieved by changing the central metal ion (Zn, Cu, Ni, and Co) in metallated porphyrins has been shown as a way to modify the gate work function. Thermal gravimetric analysis (TGA) on Zn-porphyrin shows that the molecule is stable upto 450 °C. Temperature stability experiments on MOSCAPs show that the above method can be effectively implemented in advanced CMOS technologies involving the gate-last process.

Index Terms—CMOS, interface dipole, self-assembled monolayer (SAM), work function.

I. INTRODUCTION

WITH the aggressive scaling of CMOS technology, the conventional poly-Si gate is known to suffer from short-channel effects such as polydepletion, high gate resistance, and boron penetration. Thus, new gate electrode materials, including metal gates, are being investigated to replace the traditional poly-Si gate for the 45 nm node and below CMOS technologies [1]. In this context, the importance of metal-gate work function tuning is very important for the advanced CMOS technologies. The work function tuning for metal-gate technologies has been successfully implemented using various techniques such as metal inter-diffusion, dopant implantation, silicidation, interface dipoles, nitridation, and alloying [2]. For bulk devices, the required metal work functions for replacing the conventional n- and p-poly-Si gates are about 4 and 5 eV, respectively to control threshold voltage swings. Without doubt, the use of two different metals for PMOS and NMOS devices requires complicated selective deposition and etching processes for their integration into the conventional CMOS technologies. In this work, we present a viable and inexpensive alternate solution by

use of self-assembled monolayer (SAM) of organic molecules, sandwiched between a metal and a gate dielectric, to selectively tune the work function of a specific metal [3].

Previous works have reported the use of SAMs to tune the work functions of Au, Ag metal electrodes in organic electronic devices such as polymer LEDs and photovoltaic cells. Use of SAMs of alkanethiols to manipulate the charge injection into organic FETs has been demonstrated [4]. Modification of work function of Ti (Φ_{Ti}) was achieved by self-assembled monolayer molecules of aminopropyl triethoxy silane on $\text{SiO}_2/\text{p-Si}$. The change in Φ_{Ti} was attributed to the change in the electrical potential at the Ti/SAM interface in the presence of the SAM molecules with dipole moment. It was emphasized that controlling the magnitude of the work function value has an enormous potential for the fabrication of CMOS devices, as well as possibilities to tailor the behavior of opto- and bionanodevices [3]–[5].

In our previous work, we demonstrated the use of 5-(4-hydroxyphenyl)-10,15,20-tri(p-tolyl)Zn(II) porphyrin (ZnTTP-OH) SAM as a Cu diffusion barrier for ultralarge-scale integration (ULSI) metallization and for microfluidics [6]. In this work, TTP-OH and their metal derivatives (Zn, Cu, Ni, and Co) have been used to tune the metal-gate work function. Besides excellent thickness control, the main advantage of using porphyrins is the wide range of its derivatives. We can tune the dipole moment not only by changing the central metal ion, but also by changing the groups attached to the porphyrin ring.

In the following sections, the surface morphological studies carried out using (AFM) on SiO_2 and on SAM/ SiO_2 are presented. The redox chemistry of metalloporphyrins is presented. Water contact-angle measurements were done to check the formation of above SAMs on SiO_2 . The results of density functional (DFT) simulations and UV-visible absorption spectra of metallo-TTP-OH in toluene are discussed. Thermal gravimetric analysis (TGA) is done to determine degradation temperature of porphyrin molecule. High-frequency capacitance voltage (HFCV), variable oxide thickness, and temperature-stability analysis on MOS capacitors (MOSCAPs) with SAMs show that the shift in flat-band voltage is due to the dipole moment associated with the central metal ion in the porphyrin ring.

II. EXPERIMENTATION

Fig. 1 shows the chemical structure of TTP-OH with different central metal ions. The silicon dioxide substrate used to prepare porphyrin SAM was prepared by thermally growing SiO_2 on an RCA-cleaned p-type (1 0 0) Si wafer. Then, the SiO_2 substrate was dipped in sulphochromic acid to create –OH groups

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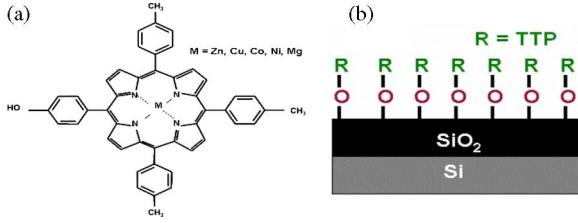


Fig. 1. (a) 5-(4-Hydroxyphenyl)-10,15,20-tri(*p*-tolyl) porphyrin with different central metal ions. (b) TTP-OH SAM on SiO_2 .

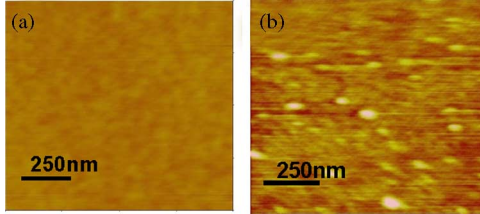


Fig. 2. Atomic force microscopy of (a) SiO_2 , and (b) Zn-TTP-OH SAM on SiO_2 .

on the SiO_2 surface by opening siloxane bonds and forming silanol groups (SiOH) on the surface. TTP-OH (with different central metal ions) was dissolved in toluene to prepare 10^{-4} M solution. The SiO_2 substrate with activated SiOH groups was dipped in the above solution for 5 min. During immersion, the head groups of the porphyrin molecule chemically bond with the silanol groups on SiO_2 surface forming a SAM [see Fig. 1(b)].

For electrical characterization, Al/ SiO_2 /Si and Al/SAM/ SiO_2 /Si MOSCAP test structures were fabricated. Al gate/back contact was deposited using thermal evaporation at a base pressure of 2×10^{-6} mbar. The MOS capacitance as a function of applied gate voltage was measured using an Agilent 4284A LCR meter. The HFCV technique was used for extracting the flat-band voltage (V_{fb}), the work function difference (Φ_{ms}) and other important electrical parameters for the test capacitors. TGA on 2.73 mg Zn-porphyrin was done while N_2 was used as initial purge gas. Temperature stability analysis on MOSCAPs was done after performing the post-metallization annealing (PMA) on the samples at different temperatures in N_2 ambient for 1 h.

III. RESULTS AND DISCUSSION

Fig. 2 shows the surface morphology of the SiO_2 films with and without SAM examined by AFM). Several $1 \times 1 \mu\text{m}^2$ AFM scans on different parts of the above samples show that the rms surface roughness of SiO_2 sample was 1.55 \AA , whereas it was 2.40 \AA in case of Zn TTP-OH SAM on SiO_2 . Clearly, the surface roughness of porphyrin SAM on SiO_2 is comparable to that of SiO_2 . The redox chemistry of metalloporphyrins was studied by cyclic voltammetry at a scan rate of 50 mV/s and differential pulse voltammetry at a scan rate of 20 mV/s using tetrabutylammonium perchlorate as supporting electrolyte (0.1 M) in dichloromethane. Different peaks in cyclic voltammograms

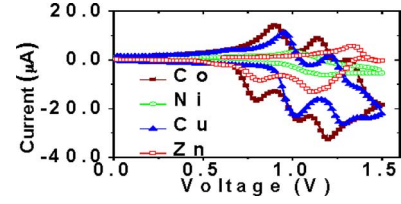


Fig. 3. Oxidation waves of cyclic voltammograms of metallo-TTP-OH.

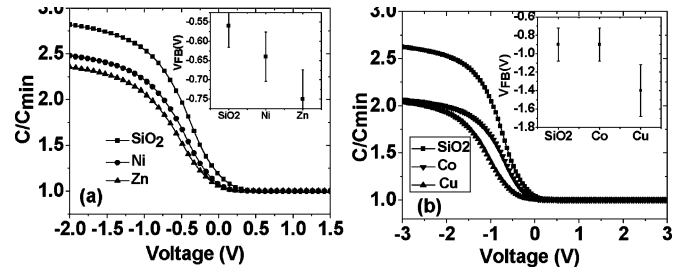


Fig. 4. Normalized (C/C_{min}) HFCV plots (a) $t_{\text{ox}} = 3 \text{ nm}$, Al/ SiO_2 /p-Si, Al/(Zn/Ni) porphyrin SAM/ SiO_2 /p-Si MOSCAPs. (b) $t_{\text{ox}} = 3.5 \text{ nm}$, Al/ SiO_2 /p-Si, Al/(Cu, Co) porphyrin SAM/ SiO_2 /p-Si MOSCAPs.

correspond to different oxidation/reduction states of central metal ion in the porphyrin ring [7]. A comparison of oxidation waves of (Zn, Cu, Ni, and Co) TTP-OH is shown in Fig. 3. TTP-OH containing Cu has oxidations at 1.02 and 1.26 V , for Ni at 0.65 and 1.09 V and for Zn at 0.80 and 1.09 V , respectively. As expected, CoTTP-OH showed three oxidations at 0.76 , 1.00 and 1.17 V . DI water ($50 \mu\text{L}$, Resistivity $\sim 18.2 \text{ M}\Omega\text{-cm}$) contact angle measurements were carried out using GBX Digidrop contact angle meter. The water drop on SiO_2 surface exhibited contact angles of $30 \pm 2^\circ$ showing hydrophilic nature of the surface. In the case of TTP-OH (with different central metal ions) SAM on SiO_2 , the contact angles were found to increase up to 78° .

Fig. 4(a) and (b) shows the C - V curves for the bare SiO_2 (3 – 4 nm thick) and the SiO_2 surface covered with TTP-OH SAM with various metal derivatives (SAM formation times similar for all the samples). The decrease in measured C_{max} or increase in total EOT is due to the formation of SAM on SiO_2 . The potential (Φ_{SAM}) across SAM modifies the surface potential at the metal/SAM interface, thereby increasing or decreasing the Φ_{metal} . Therefore, the measured metal work function is given by $\Phi_{\text{metal,mod}} = \Phi_{\text{metal}} \pm \Phi_{\text{SAM}}$ [3], [5]. Because of high π -conjugation in porphyrin, the direction of the dipole moment is from the SiO_2 surface toward Al-gate, causing a V_{fb} shift, which is toward the left in MOSCAPs with metalloporphyrin SAMs. For sample 1 with $t_{\text{ox}} \sim 3 \text{ nm}$, as in Fig. 4(a), shift observed with ZnTTP-OH SAM ($\Delta\Phi_{\text{metal}} = -0.3779 \text{ V}$, EOT = 3.58 nm) is more than that of with NiTTP-OH SAM ($\Delta\Phi_{\text{metal}} = -0.152 \text{ V}$, EOT = 3.51 nm). For sample 2 ($t_{\text{ox}} \sim 3.5 \text{ nm}$), as in Fig. 4(b), shift due to CuTTP-OH SAM (-0.258 V , EOT = 4.23 nm) is higher compared to that of CoTTP-OH SAM (-0.038 V , EOT = 4.18 nm). The measured values of interface charge densities in these MOSCAPs are in the order of 10^{11} cm^{-2} . Above results show that the shift is quite high with Zn and Cu central metal

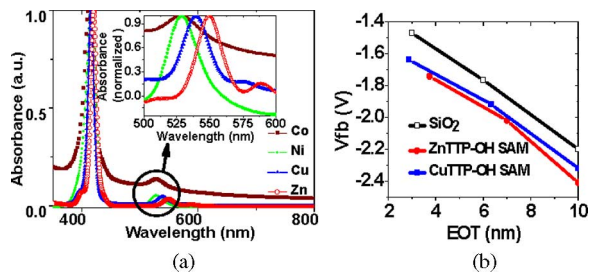


Fig. 5. (a) Ground-state UV-visible absorption spectra 1 μ M hydroxyl phenyl metalloporphyrins in toluene. Inset shows the normalized Q-band spectra and peak values for different central metals. (b) V_{fb} versus variable oxide thickness.

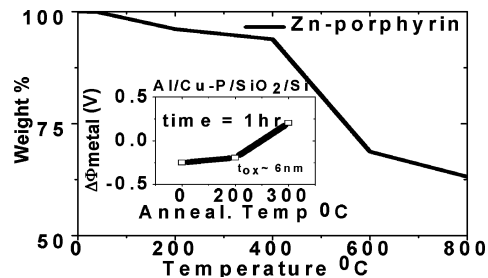


Fig. 6. TGA on Zn-porphyrin. CuTTP-OH SAM metal work function shift versus PMA temperature (inset).

ions, moderate for Ni and quite low for Co as dipole moment decreases from Zn to Co. DFT calculations on TTP and ZnTTP-OH give the values of overall dipole moments for these molecules as 0.0079 and 2.9577 Debye, respectively. The B3LYP functional and 6-31G (d) basis set have been used to study the structure and dipole moments of above molecules. Fig. 5(a) shows the UV-visible spectra of TTP-OH with different central metals. The increase in redshift of the Q bands [inset Fig. 5(a)] of TTP-OH corresponds to the contribution of central metal to the polarization and overall increase in the dipole moment values from Co to Zn metal substitution [8]. The high dipole moment for Zn is due to the efficient mixing of metal d orbitals and porphyrin orbitals. However in the case of Co, mixing of metal d orbitals and porphyrin orbitals is less efficient. Such a decrease in dipole moment with central metal ions was also observed in push-pull porphyrins and the dipole moment magnitude decreases as follows: Mg>Zn>Cu>Ni>Co [9]. Fig. 5(b) presents the flat-band voltage values for different oxide thicknesses. Constant shift in the presence of Cu or Zn TTP-OH SAM shows that the change in the magnitude of Φ_{ms} arises from the dipole moment associated with the organic monolayer. As can be seen from the shift, the dipole moment due to Zn is higher compared to Cu as expected.

TGA was done on 2.73 mg Zn-porphyrin using nitrogen as the purging gas by heating the sample from 35 $^{\circ}$ C to 1010 $^{\circ}$ C at 10 $^{\circ}$ C/min. It shows that there is a drastic weight loss between 400 $^{\circ}$ C and 600 $^{\circ}$ C, indicating that the molecules decompose at around 500 $^{\circ}$ C (see Fig. 6). Initial weight loss is due to evaporation of moisture from it. Inset in Fig. 6 presents the metal work function shift with CuTTP-OH SAM with different annealing temperatures. The shift ($\Delta\Phi_{metal}$) observed at 100 $^{\circ}$ C, 200 $^{\circ}$ C, and 300 $^{\circ}$ C is -0.25, -0.195, and 0.2 V, respectively. The shift observed for NiTTP-OH SAM MOSCAP annealed at 400 $^{\circ}$ C is observed to be 0.39 V. According to Liao and Scheiner, Zn, Cu, Ni, and Co binding energies in TPP are 6.32, 7.63, 9.94, and 10.81 eV, respectively [10], and these molecules seem suitable for integration with high-temperature Si device processing. Also, in the work by Bocian *et al.*, redox properties of porphyrin SAMs on Si were effectively used to build molecular memories that can withstand semiconductor processing conditions. These devices were shown to be stable under real-world operating conditions such as the extremes of temperature (400 $^{\circ}$ C) for extended periods (1 h) and did not degrade under large numbers of read-write cycles (10^{12}) [11].

IV. CONCLUSION

A technique to modify the magnitude of metal work function is demonstrated by changing the central metal ion (Zn, Co, Cu, and Ni) in the porphyrin SAM on SiO₂. DFT simulations and UV-visible spectroscopic measurements of porphyrin SAMs on SiO₂ show that the variation in dipole moment in porphyrins can be achieved by changing the central metal ion. HFCV, variable oxide thickness, and temperature stability analysis on MOS structures with the above SAMs show that the shift in flat-band voltage is due to the dipole moment associated with the central metal ion in the porphyrin ring, and hence, this technique has potential for applications in CMOS technologies involving the gate last processes.

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