# Threshold Voltage (V<sub>th</sub>) Tunability of pMOSFETs with Ternary Hf<sub>x</sub>Mo<sub>y</sub>N<sub>z</sub> Metal Gate and Gd<sub>2</sub>O<sub>3</sub> High-k Gate Dielectric

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## 1. Introduction

Metal gate and high-k gate dielectric are considered to instead of poly-silicon gate and silicon oxide for 45nm generation [1]. Metal gate has advantages of low gate resistance, eliminate poly depletion effect, and boron penetration issue.

In this work, the pMOSFET device with ternary  $Hf_xMo_yN_z$ metal gate and  $Gd_2O_3$  high-k gate dielectric has been demonstrated for the first time. Threshold voltage(V<sub>th</sub>) of  $Hf_xMo_yN_z/Gd_2O_3$ pMOSFET device can be tuned from -0.6 V to -0.08 V by controlling  $N_2$  flow ratio. A physical model has been proposed to explain extrinsic Fermi-level pinning at the  $Hf_xMo_yN_z/Gd_2O_3$  interface.

## 2. Experimental

The Hf<sub>x</sub>Mo<sub>v</sub>N<sub>z</sub>/Gd<sub>2</sub>O<sub>3</sub> pMOSFET devices were fabricated on a 4-in. n-type Si(100) using conventional self-aligned MOSFET process. After RCA cleaning, SiO2 with thickness of 600nm as a field oxide was thermally grown by the furnace. The definition of active area and RCA cleaning were employed followed by rf-sputter of  $Gd_2O_3$  as a gate dielectric with 6nm thickness. The  $Hf_xMo_vN_z$  metal gate electrode with different N2 flow ratio(0, 6,and 10%) were deposited by co-sputtering with pure hafnium(Hf) and molybdenum(Mo) targets in argon(Ar) and nitrogen(N<sub>2</sub>) mixtures. The sputtering dc power of both target is 250 W. The reactive pressure and the gas flow rate are 2×10-3 torr and 50 sccm, respectively. The detail metal gate and high-k process conditions were shown in Table 1. The  $Hf_xMo_yN_z$  gate electrodes were patterned by chemical wet etching to prevent dry etching damage. After gate patterning, S/D regions were formed by B<sup>11+</sup> implantation with a dose of 3×15 cm<sup>-2</sup> at 10 keV. Then, activation annealing was performed in N<sub>2</sub> ambient at 850°C for 30 sec. All of the samples were finally subjected to backside Al contact and sintering. The device key process flow was shown in Fig. 1. The Hf<sub>x</sub>Mo<sub>y</sub>N<sub>z</sub> thin film with thickness of 100nm was prepared also for the thermal stability study. The basic electrical properties were analysis by a Keithley 4200 semiconductor characterization analyzer.

## 3. Result and Discussion

#### Materials and Electrical properies Characterization

 $Hf_xMo_yN_z$  thin films were deposited with  $N_2$  flow ratio of 0, 6, and 10% for resistivity study as shown in Fig. 2. The resistivity of  $Hf_xMo_yN_z$  increased from 2.64×10<sup>-4</sup> to 5.03×10<sup>-3</sup> Ω-cm for samples without annealing as increasing N<sub>2</sub> flow ratio from 0 to 10%, respectively. After 950°C annealing, the resistivity of Hf<sub>x</sub>Mo<sub>v</sub>N<sub>z</sub> thin films were below 10<sup>-3</sup> order for all samples. It results in the possible application for metal gate electrode [2]. Moreover, the resistivity of Hf<sub>x</sub>Mo<sub>y</sub>N<sub>z</sub> tended to decreased with increasing N<sub>2</sub> flow ratio after annealing. It may be due to Hf<sub>x</sub>Mo<sub>v</sub>N<sub>z</sub> film phase change and is discussed with X-ray diffraction(XRD) later. In order to evaluate the N<sub>2</sub> and temperature effects on the phase variation, crystal orientation for the samples with N<sub>2</sub> flow ratio of 0, 6, and 10% were analyzed by XRD. Figure 3 shows the N<sub>2</sub> flow ratio effects on the crystal orientation of without and with annealing samples. From Fig. 3(a), 0% N<sub>2</sub> flow ratio sample only Hf(102) phase was observed. The phases of HfMo<sub>2</sub>(220) and MoN(200) were shown above 6% N<sub>2</sub> flow ratio. Compare to the annealing samples as shown in Fig. 3(b), the phase of the  $Hf_xMo_vN_z$  thin film with  $N_2$  flow ratio more than 6% changed form HfMo<sub>2</sub>(220) and MoN(200) to Mo<sub>2</sub>N(200). It suggests that the Hf<sub>x</sub>Mo<sub>v</sub>N<sub>z</sub> thin films were re-crystallization after high temperature annealing. Shen et al.,[3] has been reported the low resistivity was due to the re-crystallization of the Mo<sub>2</sub>N structure. It is consistent with the results as shown in the Fig. 2.

The  $Hf_xMo_yN_z$  metal gate electrode with  $Gd_2O_3$  gate dielectric of pMOSFET device has been demonstrated. Figure 4. shows the

typical transfer characteristic( $I_{ds}-V_{gs}$ ) of  $Hf_xMo_yN_z/Gd_2O_3$  pMOSFET before and after native bias temperature(NBT) stress. The NBT stress conditions of stress electric field, stress time, and stress temperature are -3 MV/cm, 3200 sec, and 75°C, respectively. Before NBT stress, the parameters of threshold voltage( $V_{th}$ ) and subthreshold swing(SS) are -0.2 V and 77 mV/dec. From the Fig. 4, there is no negative bias temperature instability(NBTI) effect after NBT stress. The output characteristic( $I_{ds}-V_{ds}$ ) of  $Hf_xMo_yN_z/Gd_2O_3$  pMOSFET with 6% N<sub>2</sub> flow ratio also demonstrated no NBTI effect, as shown in Fig. 5.

#### Nitrogen Effect on Threshold Voltage Modulation

The  $Hf_xMo_yN_z/Gd_2O_3$  capacitor with N<sub>2</sub> flow ratio of 0, 6, and 10% has been fabricated for work function modulation study. The effects of N<sub>2</sub> flow ratio on the C-V characteristics were shown in Fig. 6. A high N<sub>2</sub> flow ratio induces positive direction shift in the flat-band voltage(V<sub>fb</sub>). The V<sub>fb</sub> shift of about 0.6 V was obtained from 0 to 10% N<sub>2</sub> flow ratio. It suggested that the metal work function can be modulated by controlling N2 flow ratio. The metal work function can be affected by stress, defects, crystalline orientation, and so on. From pervious work [4], we believe that the mechanism of the modulation in work function was speculated by crystalline orientation. The Hf<sub>x</sub>Mo<sub>y</sub>N<sub>z</sub>/Gd<sub>2</sub>O<sub>3</sub> pMOSFET device with N<sub>2</sub> flow ratio of 0, 6, and 10% has been demonstrated. Figure 7 shows the typical transfer characteristic(Ids-Vgs) of HfxMovNz/Gd2O3 pMOSFET with N<sub>2</sub> flow ratio of 0, 6, and 10%. The threshold voltage(Vth) of HfxMoyNz/Gd2O3 pMOSFET device can be modulated from -0.6 to -0.08 V with increasing N2 flow ratio from 0 to 10%. The  $V_{th}$  shift of about 0.6 V with  $N_2$  flow ratio between 0 and 10%. The results were consistent with  $Hf_xMo_yN_z/Gd_2O_3$  capacitors as shown in Fig. 6. Figure 8 shows the Vth distribution of Hf<sub>x</sub>Mo<sub>v</sub>N<sub>z</sub>/Gd<sub>2</sub>O<sub>3</sub> pMOSFET device. Compare to the Hf<sub>x</sub>Mo<sub>v</sub>N<sub>z</sub>/SiO<sub>2</sub> pMOSFET device(not show), the Hf<sub>x</sub>Mo<sub>y</sub>N<sub>z</sub>/Gd<sub>2</sub>O<sub>3</sub> pMOSFET device has small V<sub>th</sub> shift between 6 and 10% N<sub>2</sub> flow ratio. It suggested that the Fermi-level pinning effect occurs at the  $Hf_xMo_yN_z/Gd_2O_3$  interface. For the  $V_{th}$  shift difference between Hf<sub>x</sub>Mo<sub>y</sub>N<sub>z</sub>/SiO<sub>2</sub> and Hf<sub>x</sub>Mo<sub>y</sub>N<sub>z</sub>/Gd<sub>2</sub>O<sub>3</sub> pMOSFET devices, we proposed a physical model to explain Fermi-level pinning effect, as show in Fig. 9. The Hf<sub>x</sub>Mo<sub>v</sub>N<sub>z</sub>/SiO<sub>2</sub> structure has little interface states (Fig. 9(a)), however the effective extrinsic interface states occurs near the valence band for  $Hf_xMo_yN_z/Gd_2O_3$  structure (Fig. 9(b)) and creates a dipole that tends to drive the band lineup toward the valence band position.

#### 4. Conclusion

The  $Hf_xMo_yN_z$  thin film has excellent thermal stability up to 950°C. The  $Hf_xMo_yN_z/Gd_2O_3$  pMOSFET device with  $N_2$  flow ratio of 0, 6, and 10% has been demonstrated. The  $V_{th}$  of the  $Hf_xMo_yN_z/Gd_2O_3$  pMOSFET device can be modulated from -0.6 V to -0.08 V by controlling  $N_2$  flow ratio. This is due to the crystal orientation effects on the work function. Moreover, there is no NBTI degradation of the  $Hf_xMo_yN_z/Gd_2O_3$  pMOSFET device. A physical model has been proposed to explain that the extrinsic Fermi-level pinning at the  $Hf_xMo_yN_z/Gd_2O_3$  interface. Ternary Hf-Mo-N thin film is a promise metal gate for the future application.

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### Reference

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Table 1 show the metal gate and high-k process condition. Fig. 1 The conventional self-aligned process flow of  $Hf_xMo_yN_z/Gd_2O_3$  pMOSFET device.



Fig. 3 The XRD patterns of  $Hf_xMo_yN_z$  thin films with different  $N_2$  flow ratio. (a)without annealing and (b)with annealing 950°C for 30sec. Without annealing sample, only shows the phases of  $HfMo_2(220)$ , MoN(200), and Hf(102). After annealing, the phases change from  $HfMo_2(220)$  and MoN(200) to  $Mo_2N(200)$ .



Fig. 5 The output characteristics ( $I_{ds}$ - $V_{gs}$ ) of  $Hf_xMo_yN_z/Gd_2O_3$  pMOSFET with 10%  $N_2$  flow ratio. The stress conditions of electric field, time, and temperature are -3MV/cm, 3200 sec and 75°C, respectively.



Fig. 8 Threshold voltage( $V_{th}$ ) distribution of  $Hf_xMo_yN_z/Gd_2O_3$  pMOSFET with 0, 6, and 10%  $N_2$  flow ratio. The threshold voltage( $V_{th}$ ) of  $Hf_xMo_yN_z/Gd_2O_3$  pMOSFET shifts from -0.6 V to -0.08 V between  $N_2$  ratio of 0 and 10%.



Fig. 6 The C-V curve characteristics of  $Hf_xMo_yN_z/Gd_2O_3$  MOS capacitor with 0, 6, and 10%  $N_2$  flow ratio. The flat-band voltage (V<sub>fb</sub>) shifts in a positive direction with increasing  $N_2$  flow ratio.

Fig. 2 Influence of  $N_2$  flow ratio on the resistivity of the  $Hf_xMo_yN_z$  thin films deposited on the silicon oxide. After annealing, the resistivity of  $Hf_xMo_yN_z$  thin film was low that without annealing due to re-crystallization.



Fig. 4 The typical transfer characteristics  $(I_{ds}-V_{gs})$  of  $Hf_xMo_yN_z/Gd_2O_3$  pMOSFET with 10% N<sub>2</sub> flow ratio. Before stress the parameters of threshold voltage(V<sub>th</sub>) and subthreshold swing(SS) are -0.2 V and 77mV/dec, respectively.



Fig. 7 The typical transfer characteristics ( $I_{ds}$ - $V_{gs}$ ) curve of  $Hf_xMo_yN_z/Gd_2O_3$  pMOSFET with 0, 6, and 10% N<sub>2</sub> flow ratio. The threshold ( $V_{th}$ ) shifts in a positive direction with increasing N<sub>2</sub> flow ratio.



Fig. 9 Schematic energy band diagram for (a) $Hf_xMo_yN_z/SiO_2$  shows little interface states and (b) $Hf_xMo_yN_z/Gd_2O_3$  shows effective extrinsic interface states near the valence band that pin the Fermi-level.