The Threshold Voltage Adjustment of Molybdenum Stack Gate by Nitrogen-Controlled Sputtering

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Abstract: - Stack MoN/Mo (110) crystallographic texture was used as metal gate for adjusting the Mo work function. We used a new approach by sputtering the MoNx/Mo films directly to form stack gate electrode by reactive with Ar and N2 gas mixture. The annealing process of the MoNx/Mo stack gate material post the sputtering changes the flatband voltage and electrical characterization.

Key-Words : Metal Gate, Stacked Gate, Sputtering.

1 Introduction

When metal oxide semiconductor field effect transistors (MOSFETs) are scaled in gate length beyond the 100 nm technology, the integration of metal gate electrodes and high permittivity (high-k) dielectrics into complementary metal oxide semiconductor (CMOS) gate stacks will be required. Gate depletion must be suppressed to reduce the electrical thickness of a gate dielectric film in CMOS devices for a high-performance logic large-scale integrated circuit. A metal gate electrode is a promising technology for sub-50-nm CMOS devices with an electrically thin gate dielectric of less than 1.0 nm, because of the negligibly small gate depletion and low sheet resistance of the electrode. Refractory metals such as tungsten [1]-[3] and titanium nitride [4]-[5], provide advantages over poly-Si because eliminated depletion effect, boron penetration and lower gate sheet resistance. The thin films of Molybdenum (Mo) had been observed to be thermally stable on a wide range of high-k dielectrics [6]-[10].

In this paper, a stacked gate (Mo/MoNx) electrodes is investigated by using nitrogen-concentration-controlled molybdenum nitride (MoNx) film which obtained by a nitrogen-controlled sputtering. The work function of MoNx films could be adjusted by the nitrogen gas-flow ratio during sputtering and post thermal annealing.

A metal gate with mid-gap work function for both NMOSFET and PMOSFET is one approach employed in a metal gate technology. The advantages for Molybdenum are its very low resistance and high melting point (>2600℃). In early publication, Mo with (110) crystallographic texture have been shown to exhibit work functions close to 5 eV and have been successfully use in the fabrication of CMOS devices with high permittivity gate dielectrics such as SiO2, Si3N4, ZrO2 and HfO2 [3]-[7]. And Mo has been observed to be thermally stable on a wide range of those dielectrics. It has been previously shown that, under specific deposition and anneal conditions, Mo on SiO2 exhibits a high work function suitable for the PMOS gate [8]. Mo has also been to be compatible with a dual-metal-gate process [9].

In this work, we used a new approach by sputtering the MoNx/Mo films directly to form stack gate electrode by reactive with Ar and N2 gas mixture. The annealing process of the MoNx/Mo stack gate material post the sputtering modified the flatband voltage and electrical characterization.

2. Experimental Procedures

Devices in this experiment were fabricated to MOS capacitors with Mo metal gate. A 7.5 nm SiO2 were grown on p-type, 4-6 Ω-cm (100) silicon wafer by dry oxidation at 900℃. Then, 10nm MoNx films were deposited on the SiO2 by reactive sputtering with Ar and N2 gas mixture. The N2 flow ratio (N2/N2+Ar) during the reactive sputtering was split into 0, 0.25, and 0.75. After that, all the wafers were continued deposited Mo film with 150 nm thickness by reactive sputtering. During reactive sputtering deposition, we used relatively low power (i.e., 100W) to minimize the damage at the underlying gate oxide. All the wafers were thermal annealed for 15min in Ar ambient at room temperature, 400℃ and 500℃ respectively. Aluminum (~ 200 nm) was deposited on the Mo/ MoNx stack gate and backside contact by evaporator. Finally, furnace thermal annealing at room temperature and 300℃ in Ar ambient. The process flow was shown in Fig.1.

- **RCA Clean**
- **Thermal Dry Oxidation**
- **Metal Gate Deposition: Mo/MoN$_x$**
  (Flow atio N_2:Ar = 0, 1/3 and 3)
- **Thermal Anneal**
  (Room temperature , 400℃ and 500℃)
- **Aluminum Deposition**
- **Furnace Thermal Anneal**
  (Room temperature and 300℃)

Fig.1 The process flow of Mo stack gate by nitrogen-controlled sputtering.

3. Results and Discussions

Fig.2 and Fig.3 were the SEM and TEM of cross section of Mo/MoNx stack gate. And Fig.4 shows that the results of X-ray diffraction (XRD) analysis on the Mo/MoNx/SiO2/Si stack gate after sputtering with different N2 to Ar gas flow ratio. Confirming the (110) orientation is achieved. The SIMS profile of nitrogen concentration with different gas flow ratio was shown in Fig.5. In Fig.6 is the maximum count of nitrogen with various gas flow ratio. In sputtering deposition, the nitrogen concentration in the stack gate increasing with the gradual higher gas flow ratio.

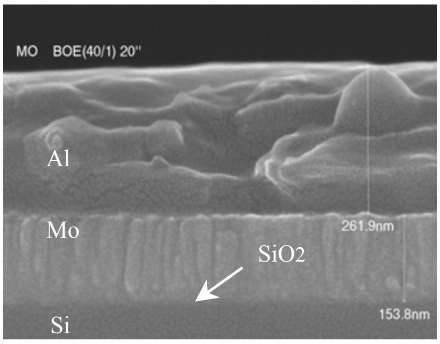

Fig.2 The SEM cross section of different Mo/MoNx stack gate.

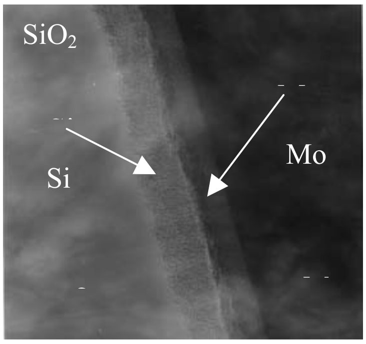

Fig.3 The TEM cross section of different Mo/MoNx stack gate.

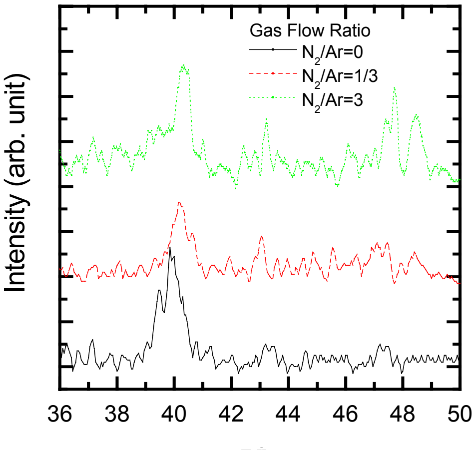

Fig.4 The XRD of different N2/Ar gas flow ratio.

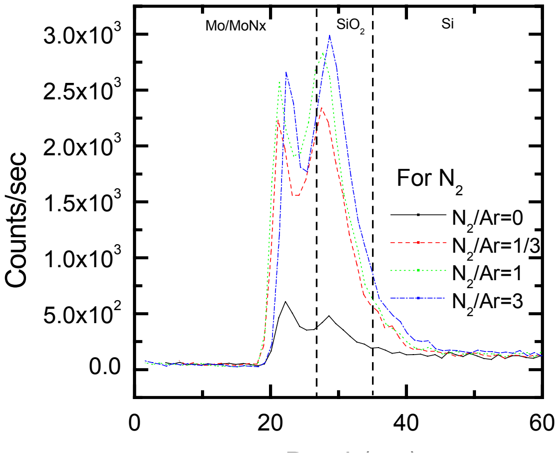

Fig.5 The SIMS of nitrogen profile in Mo/MoNx stack gate.

In order to discuss the influence of nitrogen concentration on gate sheet resistance, we employed the four-point probe to measure the resistivity of MoNx and Mo films. The results were shown in Fig.7 Obviously, the ratio of MoNx film was increasing, the resistivity was also increasing, too. The process flow of MoNx/ Mo stack gate was shown as follow. And the stack gate thickness was 120nm.

Thermal in-situ anneal and furnace anneal was testing for the thermodynamic stability of metal work function. Besides, the different Ar and N2 gas mixture sputtering would also affect the work function. The flatband voltage difference with different furnace anneal were shown in Fig.8. It is obviously that as the furnace anneal temperature was increasing, the flatband voltage was shift to the positive direction. It has been proved that nitrogen concentration could adjust the Mo work function effectively. Fig.9 was the flatband voltage that with different furnace anneal of different N2/Ar gas flow ratio. It was decreasing as the nitrogen ratio increasing. Therefore, we can determinate that the nitrogen decreased the Mo work function. Because of the nitrogen has effectively eliminated the interface state from Mo and SiO2 interface.

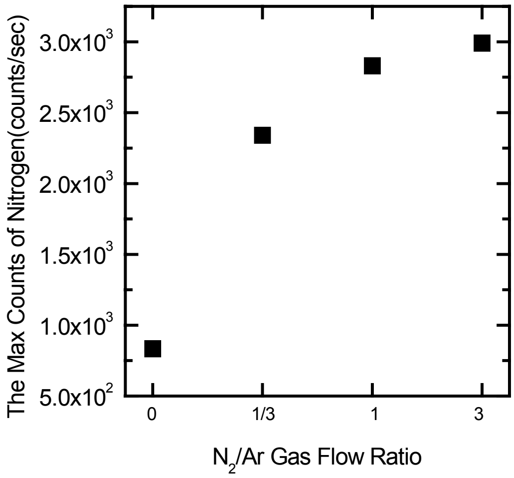

Fig.6 The maximum counts of nitrogen in different N2/Ar gas flow ratio.

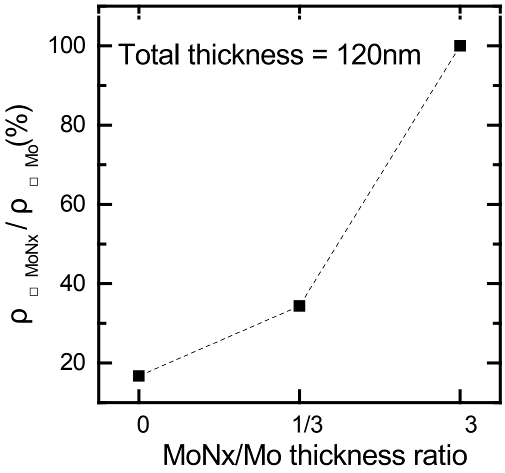

Fig.7 The sheet resistance percentage of different MoNx / Mo thickness ratio metal gate.

The energy band diagram was shown in Fig. 10. The relation of electric breakdown field and thermal in-situ anneal was shown in Fig.11. As the anneal temperature becoming higher, the electric breakdown field were also increasing. The electric breakdown field that with different thermal in-situ anneal of different N2/Ar gas flow ratio was shown in Fig.12. The electric breakdown field was increasing with the nitrogen concentration.

Fig.13 was the gate oxide leakage current (@V_G-V_{FB}=-8V) as a function of in-situ annealing condiction with different N2/Ar gas flow ratio. As the increasing of thermal in-situ anneal temperature, the leakage was lowered.

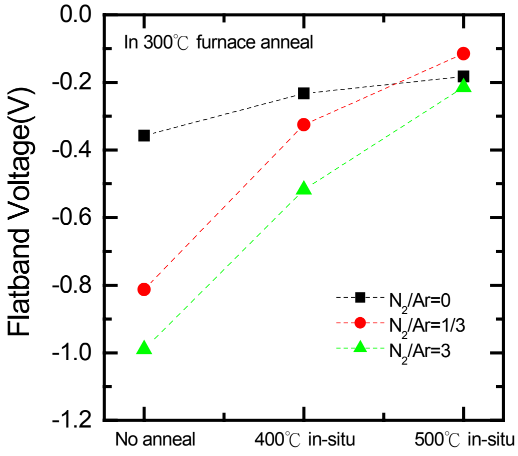

Fig.8 The flatband voltage of different N2/Ar gas flow ratio metal gate were changed in different furnace anneal temperature.

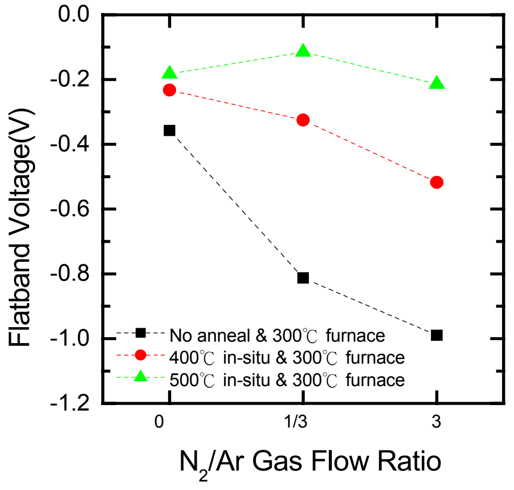

Fig.9 The flatband voltage of different furnace anneal temperature.

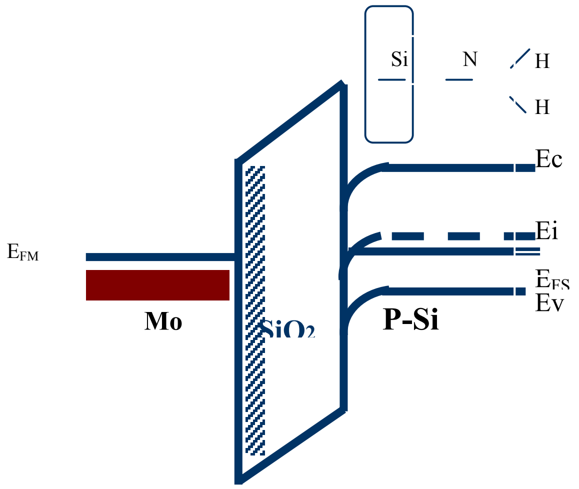

Fig.10 Energy-band diagram of Mo metal gate MOS.

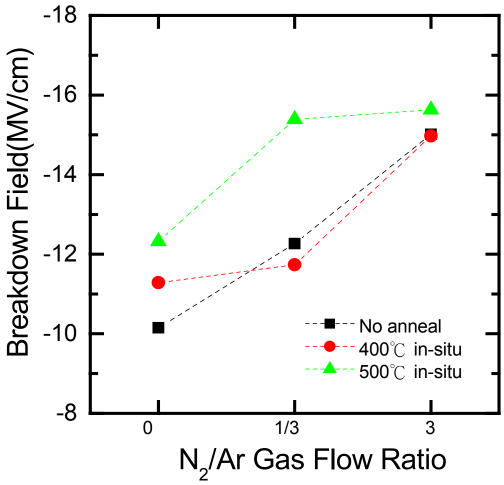

Fig.11 The electric breakdown field of different N2/Ar gas flow ratio metal gate were changed in different thermal in-situ anneal temperature.

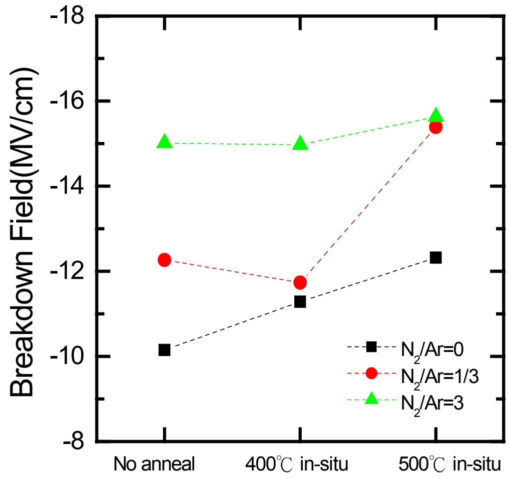

Fig.12 The electric breakdown field of different thermal in-situ anneal temperature were changed in different N2/Ar gas flow ratio metal gate.

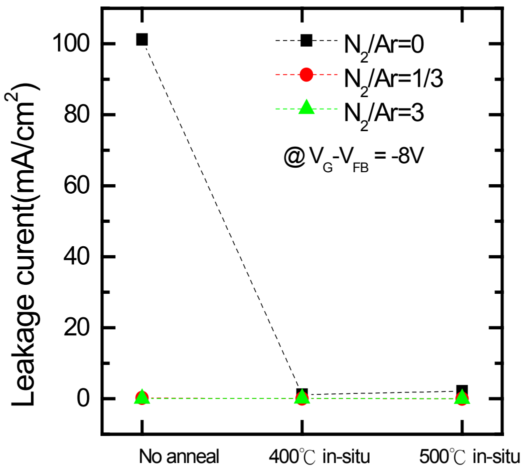

Fig.13 The oxide leakage of different N2/Ar gas flow ratio metal gate were changed in different thermal in-situ anneal temperature.

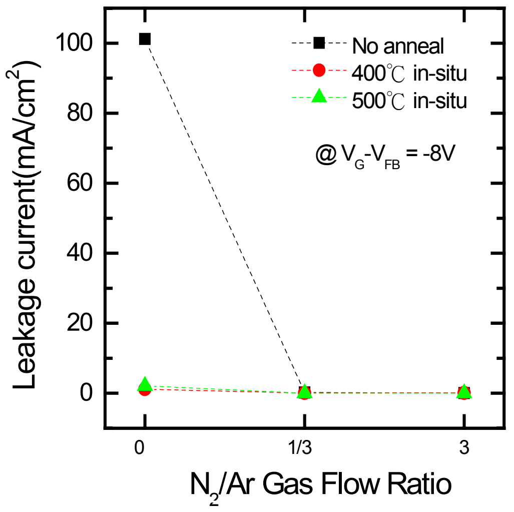

Fig.14 The oxide leakage of different thermal in-situ anneal temperature were changed in different N2/Ar gas flow ratio metal gate.

After MoNx films deposition, the leakage was also lowered which was shown in Fig.14. Because the film of MoNx were eliminated the interface to lower the oxide leakage.

4. Conclusion

In the paper, we developed the process for work function adjustment of MoN/Mo stacked gate by nitrogen-controlled sputtering. With increasing nitrogen gas flow ratio and annealed temperature, the work function was decreased. The electric breakdown field (EBD) was increased with increasing annealing temperature and nitrogen gas flow in sputtering. In the Mo/MoNx stack gate, the resistivity was increasing when increasing the nitrogen ratio of MoNx films. The Leakage current can be lowered when MoNx films were be deposited and annealed.

Acknowledgements:

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