Influence of Nitrogen Profile on Metal Workfunction in Mo/SiO₂/Si MOS Structure

Masaki Hino, Takaaki Amada, Nobuhide Maeda, and Kentaro Shibahara

Research Center for Nanodevices and Systems, Hiroshima University 1-4-2, Kagamiyama, Higashihiroshima, 739-8527, Japan

Phone: +81-824-24-6267 E-mail: hino@sxsys.hiroshima-u.ac.jp

1. Introduction

Dual-workfunction gates with a single refractory metal are expected to replace dual-poly-Si gate that accompanies a depletion effect problem. For that purpose metal workfunction tuning must be accomplished maintaining compatibility to conventional CMOS fabrication process. Though nitrogen implantation into Mo gate is known as a solution tuning the workfunction [1,2], it gives rise to damage to MOS interfaces observed as a hump shape in C-V characteristics and increase in gate leakage current [3]. Lander et al. [4] reported that nitrogen is introduced by solid -phase diffusion from a TiN film deposited on a Mo layer and workfunction can be modified.

In this paper, role of nitrogen in a $Mo/SiO_2/Si MOS$ structure for workfunction tuning is discussed through process dependence investigation of the workfunction shift and nitrogen profile evaluation.

2. Experiments

Mo workfunction is extracted from C-V characteristics of MOS diodes. Mo and TiN were deposited in turn by sputtering and reactive-sputtering methods on a thermally grown SiO₂, as shown in Fig. 1. Oxide thicknesses were 5 and 10 nm that were utilized to compensate the influence of a fixed charge in extraction of the workfunction. Nitrogen was diffused from the TiN film into an underlying Mo layer by RTA at 800°C or 900°C for 1 or 30 min. Mo gate MOSFETs were also fabricated to evaluate the workfunction from threshold voltage. Nitrogen profiles in the MOS structure were evaluated by back-side SIMS technique.

3. Results and Discussion

Figure 2 shows C-V characteristics of TiN/Mo MOS diodes. Workfunction decreased to 4.64V by 0.46V from 5.10V for a Mo gate without nitrogen incorporation. The magnitude of workfunction shift was not influenced by both annealing time and temperature. TiN composition was modified aiming to increase the workfunction shift by changing Ar/N_2 flow rate for the reactive sputtering. However, it was not affected also by the compostion TiN, as shown in Fig. 3. The features like the hump in C-V characteristics that implies interface state increase and gate current increase were not observed for TiN/Mo gate MOS diodes.

Figure 4 shows I_D - V_G characteristics of MOSFETs fabricated to observe the workfunction shift as the threshold voltage shift. However, the characteristics for the TiN/Mo gate and the Mo gate are almost identical to each other,

as shown. That means the workfunction shift observed in the MOS diodes disappeared in MOSFETs. In the case of MOSFETs fabrication, the TiN film was removed after the nitrogen solid phase diffusion prior to Mo gate patterning to reduce difficulties in RIE of TiN. In the case of MOS diode fabrication, since gate size is much larger than that for FETs and gate edges locates on thick field oxides, TiN etching is not so difficult. The influence of this process step difference was confirmed by MOS diodes fabrication with a TiN removal step shown in Fig. 5. The TiN stripping without additional thermal treatment that is called "diode process" dose not affect and the workfunction shifted like previous MOS diodes, as shown in Fig. 6. However, by annealing after the TiN stripping clearly reduced the workfucntion shift. The annealing step corresponds to activation annealing for MOSFET S/D (source and drain).

Figure 7 shows nitrogen profiles around the Mo MOS interfaces. Nitrogen pileup at the Mo/SiO₂ interface formed by the solid phase diffusion from TiN decreases by the additional annealing after the TiN stripping. Nitrogen concentration in the Mo layer was also decreased by the annealing. These results mean that the nitrogen pileup reduction due to the nitrogen out-diffusion through the Mo film is the origin of reversible workfucntion behavior. Nitrogen pileup at the SiO₂/Si interface observed for a nitrogen implanted diode is considered to be the origin of interface/oxide degradation. Figure 8 shows a model to explain the role of nitrogen at the Mo/SiO₂ interface. Because of the electron negativity difference between nitrogen and SiO₂, shown in Table 1, electrical dipoles that modify the workfunction are formed [5, 6].

4. Summary

Nitrogen pileup formed by solid-phase diffusion from TiN to Mo shifted the workfunction in a MOS system. The shift is attributed to the dipole formation at the metalinsulator interface.

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and major fabrication process conditions of TiN/Mo MOS diodes.

MOSFETs.

10²¹

10²⁰

10¹⁹

0

Nitrogen Concentration [cm⁻³]

Though V_{FB} shift was clearly observed after solid-phase nitrogen difusion from TiN into Mo, its magnitude was not influenced by annealing time and temperature.

TiN/Mo/SiO₂/Si

TiN Removal

Diode Process

No RTA

N+ Imp

RTA: Solid Phase Diffusion

800°C, 1 min

Gate Formation: Mo RIE

Fig.1 Cross sectional structure Fig.2 C-V characteristics of TiN/Mo MOS diodes. Fig.3 C-V characteristics of TiN/Mo MOS diodes. Though V_{FB} shift was was not influenced also by TiN composition modified by reactive sputtering condition.

T_{OX}: 10 nm

Mo Gate

1.0

1.5 2.0



Gate Voltage V_G [V] Fig.4 I_D-V_G characteristics of TiN/Mo and Mo Fig.5 MOS diode fabrication Fig.6 C-V characteristics of TiN/Mo MOS gate MOSFETs. Vth shift due to workfunction change was not observed in TiN/Mo gate

TiN/Mo

Diode Proc

Mo

10

FFT Proc

process flow to discuss the reason why workfunction shift disappeaed in MOSFET fabrication.

diodes. Though V_{FB} shift decreased by FET-like fabrication process shown in Fig. 5 that contains RTA after TiN removal

0 0.5

V_G [V]

Mo-SiO₂ Interface

FET Process RTA: S/D Activation

900°C. 1 min



4

3.5

3

2.5

2

1.5

1

0.5

0

TiN/Mo-

TiN/Mo

-2.0 -1.5 -1.0 -0.5

FET Process

Diode Process

Capacitance [fF/μm²]

Fig.8 Electrical dipole model to explain workfunction shift at the Mo/SiO₂ interface.



Table 1. Electron nagativity for components that consist a Mo/ SiO₂/Si MOS system.



SiO₂

20

Depth [nm]

Si

30

40