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Full Range Work Function Modulation by Nitrogen Incorporation in Hf–Mo Binary Alloys Gate Electrode

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1. Introduction

As scaling of channel length goes down to sub-45nm generation, metal gate electrode [1] has the benefit on low gate resistance, eliminate poly depletion effect and boron penetration issue. IBM had announced to use different metal gates with Hafnium(Hf)- base gate dielectric for 45nm products [2]. It is expected they have complex integrated processes with high cost. A simple and low cost metal gate process development is necessary. In this work, a metal gate with full range work function modulation process has been first time demonstrated. The Hf_xMo_y binary alloys cover the work function range from conduction to valance band (4.17~ 5.16eV). It is believed that this process has the potential to be a cost effective on N and PMOS process integration. The crystal orientation, binding energy, and thermal stability of $Hf_xMo_yN_z$ thin film was systematic investigated.

2. Experiment

Metal-oxide-semiconductor (MOS) capacitors were fabricated in this study. The SiO_2 dielectrics with thickness range form 100Å to 500Å were grown by thermal oxidation on p-type silicon substrate. After oxidation, $Hf_xMo_yN_z$ (1000Å) gate electrode was deposited by co-sputtering at DC-sputter by 250W(Hf):200W(Mo) in N_2 and Ar mixtures, with N_2 flow ratio from 0% to 14%, respectively. $Hf_xMo_yN_z$ gate was patterned by wet etching using the chemicals solution. Finally, 3000Å Al films were deposited on backside contact. The detail process flow and schematic MOS capacitors cross-section were shown in Fig.1 (a) and (b), respectively. For thermal stability study, the $Hf_xMo_yN_z$ thin films deposited on 600 nm oxides were prepared also. The capacitance-voltage (CV) curves and resistivity of $Hf_xMo_yN_z$ were measured by HP 4285 LCR meter and four point-probe meter, respectively.

3. Results and Discussion

Thermal Stability of $Hf_xMo_yN_z$ Thin Films

Fig. 2 shows the resistivity of $Hf_xMo_yN_z$ films with different sputtered N_2 flow ratio and post metal anneal (PMA) temperature. The resistivity of $Hf_xMo_yN_z$ increased from 1.84×10^{-4} to 3.1×10^{-3} Ω-cm for all nitrogen ratios and nearly not affected by PMA. It can be seen that high temperature annealing had little effect on the resistivity of the film. In order to examine thermal stability, RTA anneal were performed for all samples at 700°C and 900°C, respectively. The XRD analysis is shown in Fig. 4. In this figure, we can observe that the lower resistivity of $Hf_xMo_yN_z$ thin films were relative. And the resistivity tended to drop in high nitrogen ratio (8~14%) at 900°C . The without (W/O) anneal and 700°C anneal sample was not obvious peak for Mo_5Si_3 in Fig. 4 (a) and (b) , but the 900°C anneal sample was observed the peak of Mo_5Si_3 on XRD material analysis as shown in Fig 4 (c). It can be sure that the lower resistivity was caused by Molybdenum (Mo) silicides crystal formed in $Hf_xMo_yN_z$ films.

Material Characterization

Fig.5 (a) shows the binding energy of N(1s) peaks can be observed at 398.1eV in 4% and 12 % of $Hf_xMo_yN_z$ films. According to the comparison of these curves, there is no nitrogen peaks in XPS analysis of 0% film, and besides, the shift of the peak of nitrogen can further demonstrate its incorporation. In addition, Fig.5 (b) and (c) show that both the peaks of Mo and Hf tend to shift toward high binding energy, and that means exactly the same phenomena of nitrogen incorporation. The difference between the peak intensity of Hf(4f) of 4% and 12% is shown in Fig.5 (c). An obvious decrease of intensity of 12% Hf(4f) peak can be observed while there is no such situation in both two of Mo(3d) metal gate electrodes as shown in Fig.5 (b). The decrease of the intensity might be due to the incorporation of high nitrogen ratio [3].

Nitrogen Effect on Work Function Modification

The C-V curves of $Hf_xMo_yN_z$ /SiO_2 gate stacks with different sputtered N_2 flow ratio are shown in Fig. 6. In order to decouple the effect of oxide charge from the effective work function, the capacitors with different oxide thicknesses were fabricated to generate a V_{FB} vs. EOT curve as shown in the inset of Fig. 7. The y-intercept of this curve indicated the effective work function ($\Phi_{m,eff}$). The extracted $\Phi_{m,eff}$ values for $Hf_xMo_yN_z$ gate electrode with different N_2 flow ratio ranged from 4.17eV (low N_2) to 5.16eV (high N_2) are shown in Fig. 7. According to the reference paper [4], the work function of Hf was modified by nitrogen (N) incorporation, and indeed the work function of HfN_x can be tuned from 4.1eV (conduction band) to 4.55eV (midgap). In this work, for the first time, larger work function range than previous work is obtained forming co-sputtering $Hf_xMo_yN_z$ metal gate. In addition, the Mo film with (110) orientation can maintain possessing high work function value suitable for p-channel devices [5]. This suggests that $Hf_xMo_yN_z$ films have tunable effective work functions appropriate for both NMOS and PMOS devices. Table 1 shows relationship between crystal orientation of Mo films and work function of MOS capacitors [6].

4. Conclusions

$Hf_xMo_yN_z$ metal nitride has excellent thermal stability up to 900°C. By DC sputtering with increase N_2 flow ratio form 0% to 14%, the work function of $Hf_xMo_yN_z$ gate electrode increases from 4.17eV (conduction band) to 5.16eV (valence band). This process is good enough for nMOSFET and pMOSFET applications.

Acknowledgement

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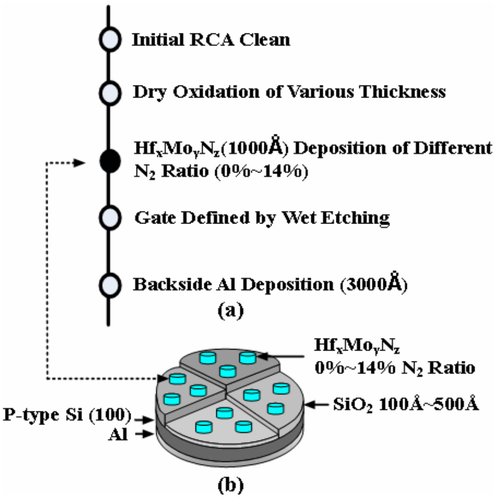

Fig.1 (a) The process flow of $Hf_xMo_yN_z$ metal gate MOS capacitors. (b) Schematic cross-section for $Hf_xMo_yN_z$ metal gate MOS capacitors in this work.

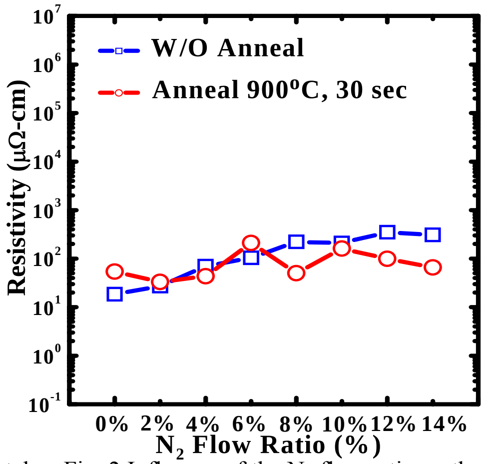

Fig. 2 Influence of the N_2 flow ratio on the resistivity of the $Hf_xMo_yN_z$ films deposited on the silicon oxide.

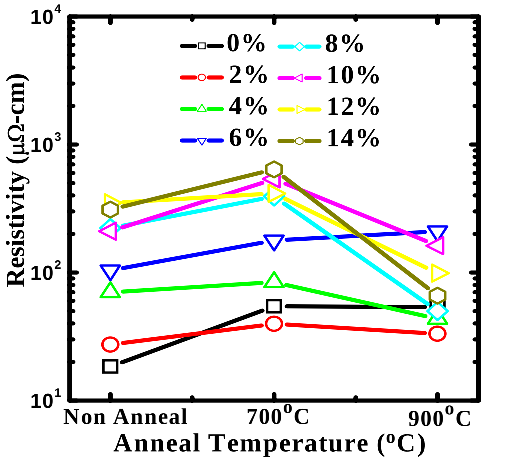

Fig. 3 The annealing temperature effects on resistivity of $Hf_xMo_yN_z$ thin films were relative.

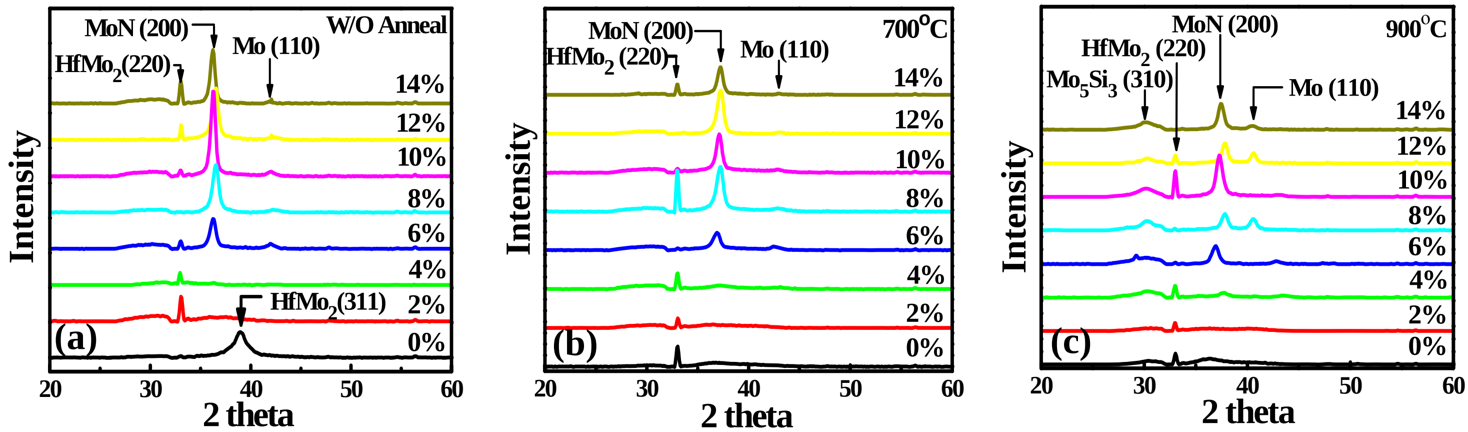

Fig. 4 XRD patterns of the $Hf_xMo_yN_z$ films with various N_2 flow ratio. (a)W/O anneal (b) Anneal 700°C, 30 sec (c)Anneal 900°C, 30 sec.

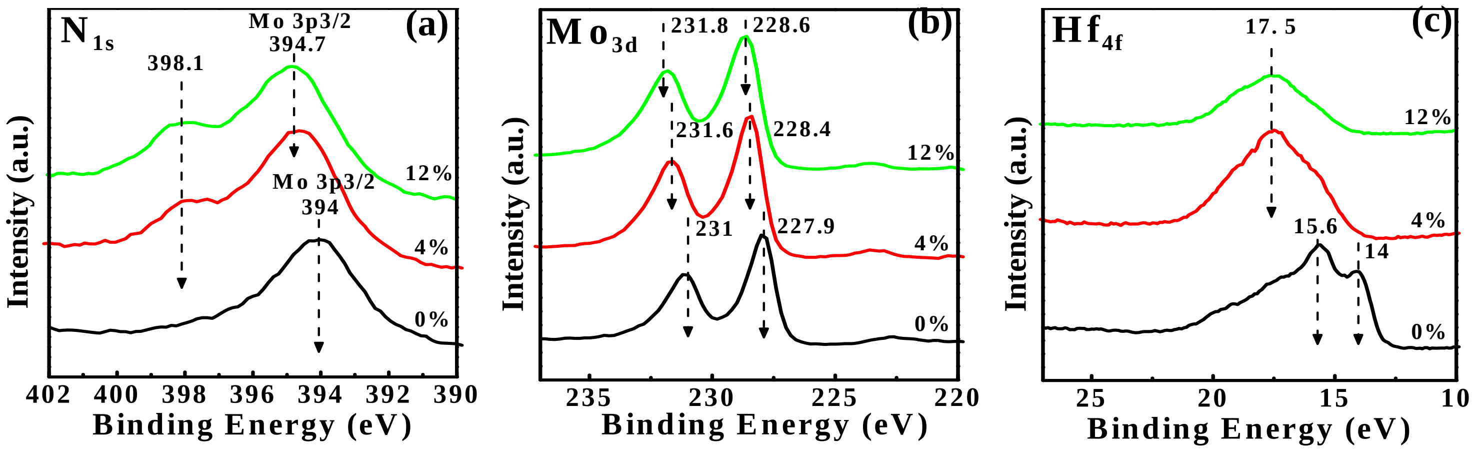

Fig. 5 XPS spectra of the $Hf_xMo_yN_z$ thin films with various N_2 flow ratio. (a): N(1s), (b): Mo(3d), (c): Hf (4f).

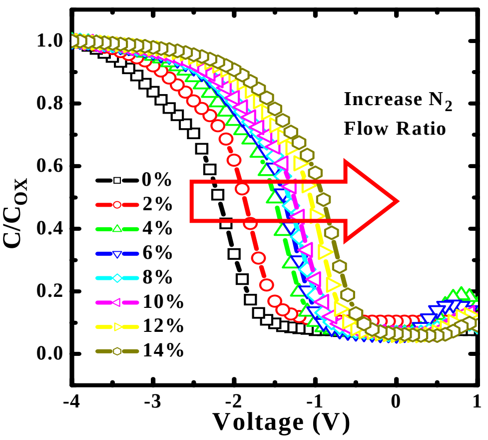

Fig. 6 Normalize C-V curves of $Hf_xMo_yN_z$ gates with various N_2 flow ratio on SiO_2/p-type Si.

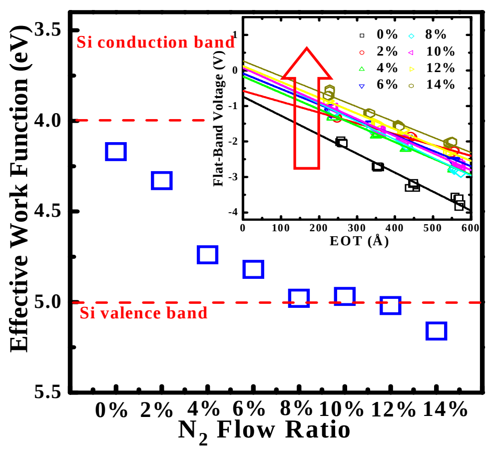

Fig. 7 Work function of $Hf_xMo_yN_z$ as a function of the N_2 flow ratio ($\Phi_{m,eff}$= 4.17eV ~5.16eV).

Table 1.
Orientation and work function of Mo gate MOS capacitors.

Material	Orientation (XRD)	Work Function (Φm)
HfN[3]	(111)	~4.1eV
	(111)&(200)	~4.55eV
Mo[5]	(100)	4.53eV
	(110)	4.95eV