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Hydrogen Ion Sensing Properties of Niobium Oxide by RTA and Thickness effect

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1. Introduction

High dielectric constant high-k materials including Al_2O_3 [1], Ta_2O_5 [2], and HfO_2 [3] have been studied to replace Si_3N_4 [4] membrane for Ion sensitive field-effect-transistors (ISFET) application due to the better stability and sensitivity. Additional advantage of high-k materials is the process compatibility for future technologies, such as the candidate for gate dielectric in CMOS and capacitance dielectric in DRAM and RF application. In this study, niobium oxide (NbO_x) which is a well-implemented material in commercial 40nm DRAM technology for cell capacitance is firstly presented to be the pH sensing membrane. Thickness of sensing membrane and post-deposition anneal (PDA) at different temperature were also investigated to find the optimized process conditions of NbO_x for pH sensing application.

2. Experimental

Single-layer Electrolyte-insulator-semiconductor (EIS) structures were fabricated to investigate hydrogen ion sensing properties. [5] NbO_x layer was deposited by radio frequency rf┐ sputtering directly on p-type (100) silicon wafer after standard RCA cleaning. The Nb target with 99.9% purity was used in reactive rf sputtering with the power of 300 W. The flow rate of Ar and O_2 was 20 and 5 sccm, respectively. The thickness of NbO_x sensing membrane was controlled by deposition time and then verified by ellipsometer measurement. Then, the PDA was performed in N_2 and O_2 ambient at temperature of 500, 700, and 900°C for 1 min, respectively. Detail process flows of all groups are shown in Fig. 1. pH sensitivities of sensing membranes were all extracted by capacitance-voltage (C-V) curves of EIS structures measured in various pH buffer solution of Merck Inc. through Ag/AgCl reference electrode by HP4284A high precision LCR meter.

3. Results and Discussion

C-V curves were measured in various standard pH buffer solutions to collect the pH-dependent C-V shift as shown in Fig. 2. pH sensitivity can be calculated by the linear fitting between the output voltage and pH value. Linearity of the fitting curve can be an index for real application in wide pH range. Totally 14 groups designed with 3 different factors including NbO_x thickness (5 and 30nm), PDA ambient (N_2 and O_2), and PDA temperature (500, 700, and 900^{o}C), respectively. In Fig. 3, the sensitivity and linearity of the group with 5nm-thick NbO_x with PDA in N_2 ambient at different temperature are presented. Low linearity which is less than 99% refers to poor response may from some minor surface damages by insufficient densification. In Fig. 4, 5nm-thick NbO_x with PDA in O_2 ambient at different temperature shows higher linearity in the group with PDA at 500 and 700^{o}C than the group without PDA and with PDA at 900^{o}C. In Fig. 5 and Fig. 6, very similar temperature dependent behavior of pH sensitivity and linearity can be observed both in N_2 and O_2 ambient. Linearity and pH sensitivity can be improved by the application of PDA at temperature from 500 to 700^{o}C. With the PDA temperature at 900^{o}C, sensitivity and linearity are slightly reduced. As shown in Fig. 7, morphology check is performed by C-AFM analysis. NbO_x or other dielectrics start to crystallize with PDA at temperature from 500 to 700^{o}C, which makes changes from amorphous type to poly-crystal type. In the meantime, surface roughness is increased by larger grain size and following larger surface area per unit square. Then pH sensitivity can be increased by more surface site density. [6] However, the grain boundaries could lead to more leakage path to makes worse stability including drift and hysteresis effect. As listed in Table 1, all pH sensing performance including drift and hysteresis can be easily compared. 5nm-thick NbO_x needs PDA in O_2 ambient to increase pH sensitivity by additional oxidation. In 30nm-thick NbO_x, drift and hysteresis can be reduced by PDA in O_2 ambient than in N_2 ambient. The optimization in this study is 30nm-thick NbO_x with PDA between 500 and 700^{o}C in O_2 ambient.

4. Conclusions

Niobium oxide is firstly investigated as a pH sensing membrane in single-layer EIS structure. To have higher pH sensitivity and linearity, PDA is suggested to perform at 500 to 700^{o}C in O_2 ambient for 30nm-thick EIS structure in real application.

Acknowledgements

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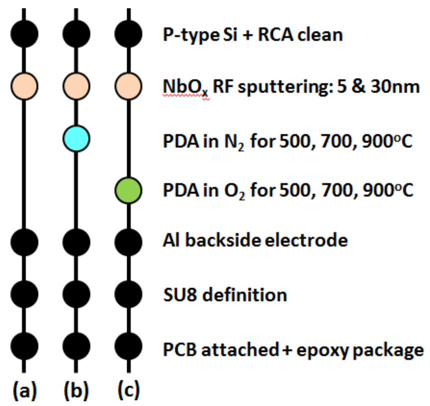

Fig. 1 Process flow of NbOx-EIS structures with (a) thickness, (b) PDA in N_2 and (c) PDA in O_2.

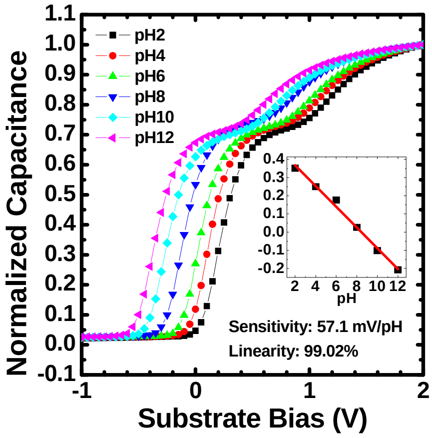

Fig. 2 C-V curves measured in various pH buff solutions of 30nm-thick NbO_x-EIS structure with PDA in N_2 ambient at 700°C.

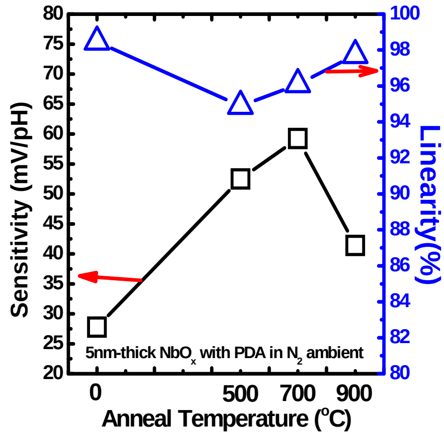

Fig. 3 pH sensitivity and linearity of 5nm-thick NbO_x-EIS structure with PDA in N_2 ambient at various temperatures.

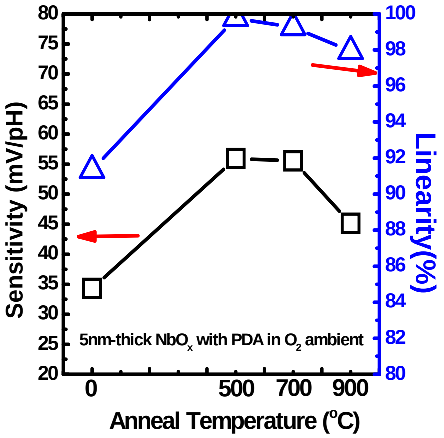

Fig. 4 pH sensitivity and linearity of 5nm-thick NbO_x-EIS structure with PDA in O_2 ambient at various temperatures.

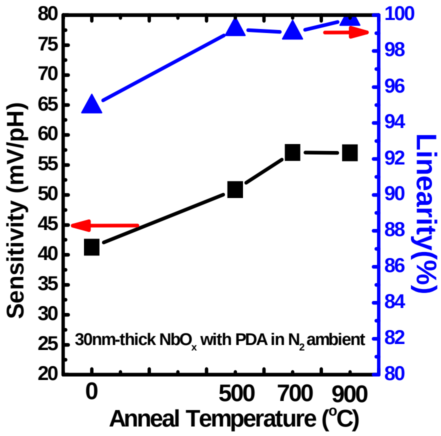

Fig. 5 pH sensitivity and linearity of 30nm-thick NbO_x-EIS structure with PDA in N_2 ambient at various temperatures.

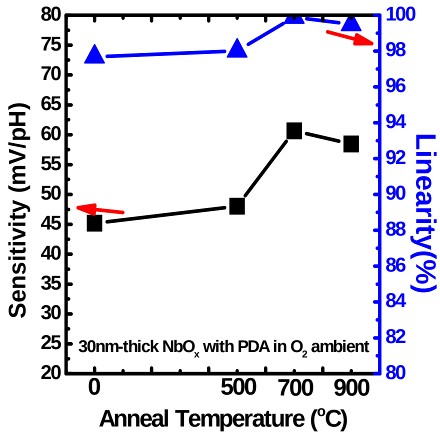

Fig. 6 pH sensitivity and linearity of 30nm-thick NbO_x-EIS structure with PDA in O_2 ambient at various temperatures.

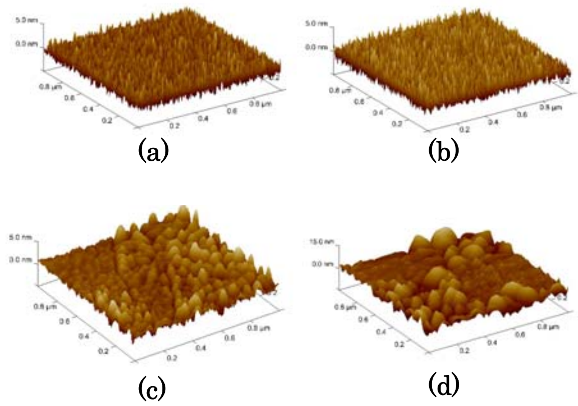

Fig. 7 AFM analysis on 30nm-thick NbO_x with PDA in N_2 ambient at (a) 0, (b) 500, (c) 700, (d) 900°C.

Table 1 Comparison on pH sensing properties of NbO_x-EIS structure by all experimental groups.

Thickness (nm)	PDA ambient	Temp. (°C)	Sensitivity (mV/pH)	Linearity (%)	Drift (mV/h)	Hysteresis (mV)
5	w/o	0	27.8	98.46	-3.1	-79.0
	N_2	500	26.7	95.76	-3.6	10.8
		700	58.3	98.91	-1.9	5.8
		900	38.1	96.92	-1.7	20.6
	O_2	500	55.9	99.76	-4.0	1.0
		700	55.5	99.26	-6.9	7.2
		900	45.1	97.93	-4.5	2.1
30	w/o	0	41.3	94.91	-4.7	-11.8
	N_2	500	50.9	99.21	-3.3	26.9
		700	57.1	99.02	-4.6	47.0
		900	57.0	**99.79**	**-5.8**	15.1
	O_2	500	53.5	**99.95**	**-0.6**	**3.6**
		700	**60.7**	**99.90**	**-2.2**	11.3
		900	58.5	**99.49**	-2.6	-3.7