Hydrogen and Alkali Ion Sensing Properties of Ion Implanted Silicon Nitride Thin Film

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B, P, and Cs ions were implanted with various parameters into silicon nitride layers prepared by LPCVD. In order to get the maximum impurity concentration at the silicon nitride surface, a high temperature oxide (HTO) buffer layers was deposited prior to the implantation. Alkali ion and pH sensing properties of the layers were investigated with an electrolyte-insulator-silicon (EIS) structure using high frequency capacitance-voltage (HF-CV) measurements. The ion sensing properties of implanted silicon nitrides were compared to those of as-deposited silicon nitride. B and Cs co-implanted silicon nitrides showed a pronounced difference in pH and alkali ion sensing properties compared to those of as-deposited silicon nitride. B or P implanted silicon nitrides in contrast showed similar ion sensitivities like those of as-deposited silicon nitride.

Keywords : Silicon nitride, Ion implantation, Ion sensitivity, ISFET (Ion sensitive field effect transistor)

1. INTRODUCTION

Silicon nitride has been successfully established as a sensitive layer for pH-ISFETs[1-3]. Silicon nitride based pH-ISFETs can be used not only for pH-detection in liquid, but also as a transducer for bio sensitive ISFETs on which relevant bio sensitive layers are immobilized [4,5]. Due to its excellent property as an ion-migration barrier and the firmly established fabrication technique that is fully compatible with conventional IC processes, silicon nitride film is a preferred material for the above-mentioned applications.

Wong et al. implanted boron ions with several doses into silicon nitride layers in order to improve their alkali ion sensing properties, where the highest boron dose implanted in the silicon nitride was 1×10^{16} cm^{-2}. But they have observed only a minute improvement of sodium and potassium ion sensitivities even for the silicon nitride implanted with the highest boron dose. Therefore, the enhancement of the alkali ion sensitivity of silicon nitride by boron implantation seems to be undesirable and other implantation impurity seems to be required. On the other hand, their implantation process was not optimized to get a maximum concentration of implanted boron at the surface of the silicon nitride layer.

Although the theory of Eisenmann[6] has been originally derived for examination of ion selectivity of bulk alkali aluminosilicates used in alkali ion sensitive glass electrodes, hypotheses from his theory can be applied to the investigation of ion selectivity of other inorganic materials. Anion field strength of surface sites of inorganic materials can be modified by implanting various impurities, which results in an alteration of potential selectivity constant of ion implanted inorganic layers.

In this paper, silicon nitride layers were deposited by a low pressure chemical vapor deposition (LPCVD) process[14] on thermally grown silicon dioxide layers. B and P ions were separatedly implanted, and B and Cs ions were also co-implanted into the silicon nitride layers. Alkali ion and pH sensing properties of the layers were investigated with an electrolyte-insulator-silicon (EIS) structure using high frequency capacitance-voltage (HF-CV) measurements. Differences of alkali ion and pH sensing properties of as-deposited and ion implanted silicon nitride layers were investigated.

2. EXPERIMENTAL

2.1 Fabrication of test structure

(100) p-type silicon wafers with a resistivity of 4-6 Ω-cm

were thermally oxidized at 950 °C up to 50 nm thickness. 60-100 nm thick silicon nitride layers were then deposited at 700 °C by LPCVD. In order to get the maximum concentration of implanted impurities at the surface of the silicon nitride, a high temperature oxide (HTO) was subsequently deposited by LPCVD additionally on the silicon nitride layers.

The thickness of the HTO layers corresponded to the projected range R_p of B, P, and Cs ions in silicon dioxide at the selected implantation energy[7]. B or P ions were implanted with 40 keV and various doses through the HTO layers into the silicon nitride layers. B and Cs ions were co-implanted in the same structures. In order to minimize the 'knock-on' effects, Cs ions were implanted with 50 keV before the B ion implantation with an energy of 10 keV. The implantation parameters and the related thickness of the HTO layers are summarized in Table 1.

Table 1. The implantation parameters and thickness of HTO layers for the B, P, and B/Cs ion implantation process.

Ions	Implantation Parameters [Energy & Dose]	Thickness of HTO
B	40 keV 1×10^{14}, 1×10^{15}, 1×10^{16}, 5×10^{16} cm^{-2}	180 nm
P	40 keV 1×10^{14}, 1×10^{15}, 1×10^{16}, 5×10^{16} cm^{-2}	60 nm
B+Cs	B: 10 keV, 5×10^{16} cm^{-2} Cs: 50 keV, 7×10^{15}, 2×10^{16}, 8×10^{16} cm^{-2}	40 nm

After the B, P, Cs ion implantation, the HTO buffer layer was etched using a buffered hydrofluoric acid (BHF: 12.5 vol.% of 50 % HF + 87.5 vol.% of 40 % NH_4F). The B or P implanted silicon nitride layers were then annealed for 20 min at 750 °C in a N_2 atmosphere in order to cure the radiation damage caused by ion implantation. Because the doses of the B and Cs co-implanted silicon nitride layer were much higher, they were annealed by rapid thermal annealing (RTA) process for 20 sec at 1000 °C in a N_2 atmosphere. On the backside of the wafers, Al thin films (500 nm) were then deposited by thermal evaporation to create an ohmic contact. In Fig. 1, cross sectional schematics of the test structures during ion implantation and at the end of the process are shown. respectively.

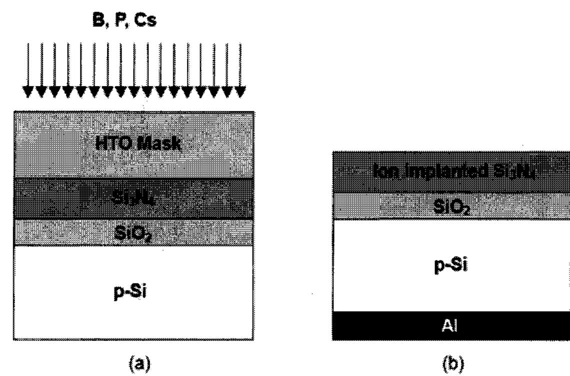

Fig. 1. Cross section of the test structures; (a) during ion implantation, (b) at the end of the fabrication process.

2.2 Characterization of ion implanted layers and test structures

It is generally known that a naturally grown thin oxide layers exists on the surface of silicon nitride layers[8]. Before the measurements, therefore, one of two silicon nitride samples with same doping condition was treated with 5 % HF for about 1 min, in order to remove the thin oxide layer from the silicon nitride surface. HF treated samples were then mounted in a measuring cell, in which the test structures were sealed by an O-ring and contacted with a buffer electrolyte.

The (desired) pH values in range between pH 3 and pH 11 in the buffer electrolyte liquid were set by injecting specified quantities of 1 M HCl and 1 M KOH with computer controlled micro pumps. Alkali ion concentration of the buffer electrolyte liquid in a range between 10^{-5} M and 10^{-1} M was set by injecting specified quantity of 1M NaCl, KCl, RbCl, and CsCl prepared in the buffer electrolyte. A magnetic stirrer was used to mix the solution.

Characterization of ion sensing properties of the test structures was carried out by HF-CV measurements with the above-mentioned configuration, where the frequency and the signal amplitude were 1 kHz and 20 mV, respectively. A preset value of a capacitance was selected from the maximum capacitance slope region on the C-V curve of the test structures. The voltage was applied to a conventional glass reference electrode (Ag/AgCl/3M KCl, *Ingold*, *Germany*). The voltage variation needed to maitain this preset capacitance value was monitored as a function of the ion concentration.

3. RESULTS AND DISCUSSION

It has been reported that as-deposited silicon nitride showed very high pH sensitivity and nearly negligible

alkali ion sensitivity[9-11]. The as-deposited silicon nitride layer in this report also showed a high integral pH sensitivity of about 57-58 mV/pH and only a minute alkali ion sensitivity, which is similar to the value reported by other authors[10,12]. The integral pH-sensitivity here is defined as the slope of a linear regression line fitted to the data in the measured pH range.

In Table 2, the integral pH sensitivities of as-deposited and ion implanted silicon nitride layers are presented. Regardless of the implanted dose, B or P implanted silicon nitride layers show nearly the same integral pH sensitivity as that of as-deposited silicon nitride layer. This is true for samples with and without the 1 min pre-treatment in 5 % HF.

Table 2. The integral pH sensitivities of as-deposited and ion implanted silicon nitride layers for etched (5 % HF) and unteched test structures. The pH titration was done from pH 3 to pH 11 and then back from pH 11 to pH 3.

Layers	Integral pH sensitivity mV/pH	
	etched	unetched
as-deposited Si_3N_4	57-58	46-47
B($1\times10^{14}cm^{-2}$) implanted Si_3N_4	57.4	48.2
B($1\times10^{15}cm^{-2}$) implanted Si_3N_4	56.6	46.8
B($1\times10^{16}cm^{-2}$) implanted Si_3N_4	58.4	45.3
B($5\times10^{16}cm^{-2}$) implanted Si_3N_4	57.9	45.9
P($1\times10^{15}cm^{-2}$) implanted Si_3N_4	58.3	48.6
P($1\times10^{16}cm^{-2}$) implanted Si_3N_4	58.6	48.5
B($1\times10^{14}cm^{-2}$)-Cs($7\times10^{15}cm^{-2}$) co-implanted Si_3N_4	54.6	33.2
B($1\times10^{14}cm^{-2}$)-Cs($2\times10^{16}cm^{-2}$) co-implanted Si_3N_4	54.5	33.9
B($1\times10^{14}cm^{-2}$)-Cs($8\times10^{16}cm^{-2}$) co-implanted Si_3N_4	54.5	35.6

All the B and Cs co-implanted silicon nitride show distinctively lower pH sensitivities than those of as-deposited and B or P implanted silicon nitride layers. The differences of pH sensitivity are more pronounced for the case of unetched silicon nitride. While the integral pH sensitivities of the other unetched silicon nitride are 45-48 mV/pH, the integral pH sensitivities of the unetched B and Cs co-implanted silicon nitride layers are 33-35 mV/pH. In addition, the differences of the integral pH sensitivities between the unetched and etched cases are 20 mV/pH for B and Cs co-implanted silicon nitride, while they are ~10 mV/pH in case of the test structures with as-deposited silicon nitride.

Considering the integral pH sensitivity (45.9 mV/pH, unetched) of the silicon nitride layer implanted with the highest B dose (5×10^{16} cm^{-2}), the lower pH sensitivities (33-35 mV/pH, unetched) of B and Cs co-implanted silicon nitride layers seem to be caused by implanted Cs ions. Among the different B and Cs co-implanted silicon nitrides, no remarkable difference in pH sensitivity was observed. A possible explanation for this behavior is that the co-implanted B and Cs atoms cause an enhanced oxidation on the silicon nitride surface, which results in a reduced pH sensitivity of B and Cs co-implanted silicon nitride layers.

In addition, a remarkable difference in hysteresis on the pH titration (pH 3 ↔ pH 11) curve was observed between as-deposited and B and Cs co-implanted silicon nitride layers. While the hysteresis at pH 7 of as-deposited silicon nitride layer was ~40 mV, the hysteresis at pH 7 of B and Cs co-implanted silicon nitride layers was 80-100 mV. These results imply that the silicon nitride layers have lost their intrinsic characteristics of a good pH sensing property through implanted impurities.

Despite the difference in implanted doses, B or P implanted silicon nitride layers showed a nearly negligible Na^+, K^+, Rb^+, and Cs^+ sensitivity. These results correspond to the similar pH sensitivities of as-deposited and B or P implanted silicon nitride layers. A small enhancement of alkali ion sensitivity was only observed for the sample with the highest B dose of 5×10^{16} cm^{-2}. They were ~10 mV/pNa in a range from pNa 3 to pNa 1, which is similar to that of the B implanted silicon nitride reported by Wong et al.

Etched (5 % HF, 1 min) B and Cs co-implanted silicon nitride layers showed a minute increase of alkali ion sensitivities compared to the etched as-deposited silicon nitride layer. On the contrary, all the unetched B and Cs co-implanted silicon nitride layers showed a remarkable difference in Na^+, K^+, Rb^+, and Cs^+ sensitivity from the other unetched silicon nitride layers, which means that the enhancement of alkali ion sensitivities of the B and Cs co-implanted silicon nitride layers were related to the thin oxide layers on their surface. In Fig. 2-5, pNa, pK, pRb, and pCs sensitivities of the B and Cs co-implanted silicon nitride layers are compared to that of as-deposited silicon nitride layer. To have a comparison of the cation sensitivity without influence of variances in the electrolyte contact area and the fixed charge in the insulators, the signal at pIon=6 was arbitrary set to 0 mV.

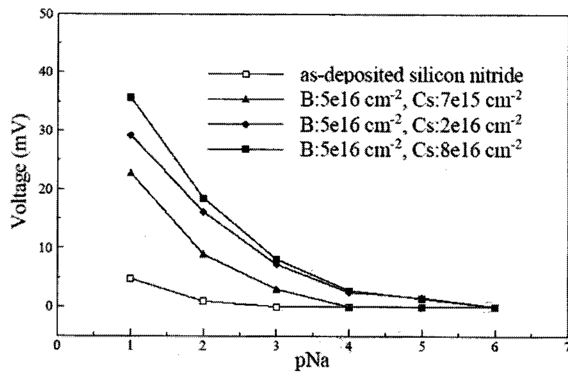

Fig. 2. pNa-titration curves for B and Cs co-implanted silicon nitride layers and as-deposited silicon nitride layers. The titration was done from pNa 5 to pNa 1. Voltages at pNa 6 of all the samples were set to 0 mV in order to compare the sensitivities to each other without influence of variances in the electrolyte contact area and the insulator charge in the silicon nitride layers.

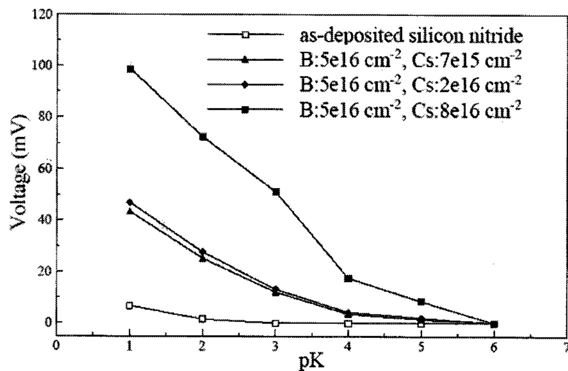

Fig. 3. pK-titration curves for B and Cs co-implanted silicon nitride layers and as-deposited silicon nitride layers. The titration was done from pK 5 to pK 1. Voltages at pK 6 of all the samples were set to 0 mV in order to compare the sensitivities to each other without influence of variances in the electrolyte contact area and the insulator charge in the silicon nitride layers.

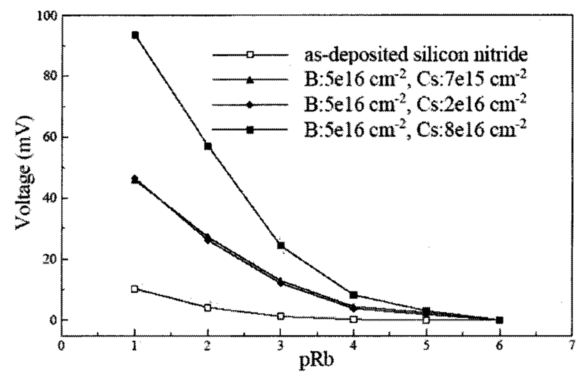

Fig. 4. pRb-titration curves for B and Cs co-implanted silicon nitride layers and as-deposited silicon nitride layers. The titration was done from pRb 5 to pRb 1. Voltages at pRb 6 of all the samples were set to 0 mV in order to compare the sensitivities to each other without influence of variances in the electrolyte contact area and the insulator charge in the silicon nitride layers.

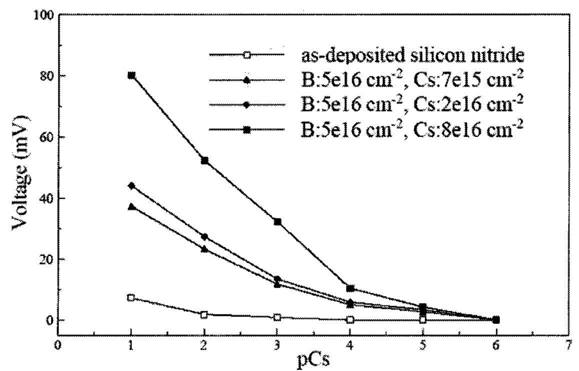

Fig. 5. pCs-titration curves for B and Cs co-implanted silicon nitride layers and as-deposited silicon nitride layers. The titration was done from pCs 5 to pCs 1. Voltages at pCs 6 of all the samples were set to 0 mV in order to compare the sensitivities to each other without influence of variances in the electrolyte contact area and the insulator charge in the silicon nitride layers.

While the as-deposited silicon nitride starts to show alkali ion sensitivities only at pIon 1, the B and Cs co-implanted silicon nitride layers show alkali ion sensitivities already at pIon 5. Contrary to the similarity of magnitudes of pH sensitivities, the B and Cs co-implanted silicon nitride layers show distinct differences in alkali ion sensitivities to each other. Overall alkali ion sensitivities of B and Cs co-implanted silicon nitride layers seem to be dependent on the dose of the implanted Cs ions. So the silicon nitride layer co-implanted with the highest Cs dose shows the highest alkali ion sensitivity among the co-implanted layers in this report. In Table 3, the integral alkali ion sensitivities of the B and Cs co-implanted silicon nitride layers in a range of pIon 3 - pIon 1 are compared.

All the B and Cs co-implanted silicon nitride layers show the highest sensitivity for K^+ or Rb^+, while they show the lowest sensitivity for Na^+. Their sensitivities for Cs^+ are between those for K^+($\fallingdotseq Rb^+$) and for Na^+. In case of as-deposited silicon nitride layer, its alkali ion sensitivity is in a relative order of Rb>Cs>K>Na. These results give us indirect information on a selectivity of the silicon nitride layers for a specific alkali ion. The B and Cs co-implantation caused a distinct improvement on the alkali ion selectivity of silicon nitride layers.

Table 3. The integral alkali ion sensitivities of B and Cs co-implanted silicon nitride layers in a range of pI 3 - pI 1.

	Integral sensitivity (mV/pI)		
	B(5×10^{16} cm^{-2}) & Cs(7×10^{15} cm^{-2})	B(5×10^{16} cm^{-2}) & Cs(2×10^{16} cm^{-2})	B(5×10^{16} cm^{-2}) & Cs(8×10^{16} cm^{-2})
Na+	6.7	8.9	11.3
K+	9.7	10.3	28.6
Rb+	10.3	10.4	26.8
Cs+	8.2	9.7	21.6

Considering the difference of alkali ion sensitivity between etched and unetched test structures with B and Cs co-implanted silicon nitride layers, the improvement of their alkali ion sensitivities is not caused wholly by intrinsic surface binding of implanted impurities with silicon nitride, but rather principally by surface binding of implanted impurities with an natural oxides on the silicon nitride layers, where the co-implanted B and Cs atoms cause most probably chemical bindings with oxygen in this thin natural oxide.

4. SUMMARY AND CONCLUSION

Despite the differences of implanted doses, B or P implanted silicon nitride layers showed similar pH and alkali ion sensitivities to those of as-deposited silicon nitride layer. Additional implantation of Cs caused distinct variance of pH sensitivities of silicon nitride layers. Thus, all the B and Cs co-implanted silicon nitride layers showed distinctively reduced pH sensitivities (33-35 mV/pH) compared to that of as-deposited silicon nitride layer. More remarkable variances have been observed in hysteresis of pH-titration curves of the B and Cs co-implanted silicon nitride layers.

Corresponding to the results of pH sensitive properties, all the B and Cs co-implanted silicon nitride layers showed remarkably improved alkali ion sensitivities compared to as-deposited silicon nitride layer. Their alkali ion sensitivities were dependent on dose of the implanted Cs ions. But their alkali ion sensitivities (11-28 mV/pI) were still quite low in order to be used as an alkali ion sensitive layer for ISFETs (Ion Sensitive Field Effect Transistors). In addition, they were more selective towards H^+ over alkali ions. The improvement of alkali ion sensitivities of the B and Cs co-implanted silicon nitride layer is probably caused by modification of a thin natural oxide on the silicon nitride layers.

Considering the relative high implantation doses adopted in this report, silicon nitride layer would not be modified to a reliable alkali ion sensitive layer through B, P and Cs implantation. Even though the results taken from this investigation can be applied to a systematic study for site-binding theory[12,13].

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