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Improving the Drift and Hysteresis of the Si_3N_4 pH Response Using RTP Techniques

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Previous work has shown that the pH sensitivity of Si_3N_4 can be increased using rapid thermal processing (RTP) techniques. In this study, the effect of an RTP treatment on the drift and hysteresis of Si_3N_4 is investigated. Results indicate that RTP-treated nitride surfaces exhibit a slow response which is very different from that of an 'as-grown' nitride surface. The response of the treated sample increases with time and eventually approaches an equilibrium value while that of the as-grown sample continues to drift upwards within the measured time period. Hysteresis measurements indicate that the magnitude of the hysteresis is reduced significantly after an RTP treatment. Non-standard hysteresis curves are frequently obtained for the as-grown nitride and this is thought to be related to the higher drift value exhibited by this surface. It is shown that the presence of hysteresis also lowers the pH sensitivity of the Si_3N_4 surface. It is proposed that the improvement in both drift and hysteresis values brought about by the RTP treatment is due to an increase in the amine/silanol ratio and possibly an increase in the overall number of amine sites at the nitride surface.

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1. Introduction

Si_3N_4 is used extensively as a pH-sensitive surface in ion-sensitive field-effect transistors (ISFETs). However, in order for Si_3N_4 to exhibit a pH response which approaches the Nernstian response of 59 mV/pH (at room temperature), a treatment in hydrofluoric acid (HF) is often required immediately prior to use.(1) An alternative method for increasing the pH sensitivity has been described previously which involves modification of the nitride surface using rapid thermal processing (RTP) techniques.(2) In that work the average value of pH sensitivity exhibited by as-grown Si_3N_4 was found to be 40–45 mV/pH. After an RTP treatment the pH sensitivity increased by approximately 10 mV/pH. It was therefore concluded that a method of increasing the pH sensitivity had been developed which did not interfere with standard processing techniques and, more importantly, eliminated the need for a HF treatment.

To determine the effectiveness of this new technique, other ISFET parameters need to be investigated. According to Bousse *et al.*(3) two mechanisms limit the accuracy with which an ISFET can be used to measure pH. These are drift and hysteresis. For HF treated Si_3N_4, drift values of 0.1–1 mV/h and hysteresis values of 3–10 mV have been reported.(4–7) Bousse *et al.*(5,6) have carried out detailed investigations of the drift and hysteresis of Si_3N_4 and have observed that, after a pH step, a Si_3N_4 surface exhibits a slow response after the initial fast response. The hysteresis is found to be a function of the time constants and the amplitude of this slow response. They also note that because values for long term drift are much less than those for hysteresis, the accuracy of the sensor is primarily affected by hysteresis.

Therefore, in this paper the drift and hysteresis of both as-grown and RTP-treated LPCVD nitride surfaces are studied and compared.

2. Theory

The sub-Nernstian pH sensitivity response of Si_3N_4 has been attributed to the presence of an oxide on its surface.(8) The effect of HF etching is to remove this oxide and therefore restore a Si_3N_4 surface with an increased pH sensitivity. The tendency of Si_3N_4 surfaces to oxidize has been investigated by a number of groups but there has been some controversy as to whether the native oxide film that forms in air at room temperature on Si_3N_4 is silicon oxynitride (SiO_xN_y) or SiO_2.(9,10) More recently, Obruji and Jayne(11) conclude that, because H^+ and OH^- cooperate to catalyse the conversion of SiO_xN_y to SiO_2, as proposed by Habraken and Kuiper,(12) the moisture in the atmosphere will promote the formation of SiO_2 over SiO_xN_y as the oxidation product of Si_3N_4.

It has been suggested by Elferink *et al.*(13) that in an ammonia ambient there is a local transition from the oxide to the nitride structure. This nitridation of the oxide results in an increase in the number of amine ($SiNH_2$) groups at the surface and therefore an increase in the amine/silanol ratio. As observed in our previous study of the RTP effect on a Si_3N_4 surface,(2) an increase in this ratio results in an increase in the pH_{pzc} (pH at the point of zero charge) of that surface and therefore an increase in pH sensitivity. This is in agreement with simulations by Meixner and Koch[14] and also with the observation that, after a HF etch, the pH_{pzc} of the Si_3N_4 surface increases.[15] In order to investigate the composition of the nitride surface after an RTP treatment, surface analysis techniques such as X-ray photoelectron spectroscopy (XPS) have been used.[16] Even though it is difficult to accurately determine the surface composition, XPS indicated that the RTP treatment increased the N/O ratio at the surface. We therefore conclude that an RTP treatment results in a chemical change at the top surface layer of the nitride with the overall effect being an increase in pH sensitivity without the need for a HF treatment.

3. Materials and Methods

To investigate the Si_3N_4 gate material of the ISFET, electrolyte-insulator-semiconductor (EIS) heterostructures were fabricated as described in ref. 2. The RTP treatment was performed in an AST-100 RTP system where a wafer was held in a single-wafer quartz chamber at atmospheric pressure. The nitride surface was irradiated using a lamp source and a pyrometer monitored the wafer temperature. The temperature/time experience of the wafer followed a pre-programmed schedule. For this work the schedule involved heating the wafer to a temperature of 1100°C for 120 s in an ammonia ambient.

Two different structures were investigated: an as-grown LPCVD Si_3N_4 surface (as-grown) and an RTP treated surface (treated). Capacitance measurements (full details of which are available in ref. 2) were performed in order to determine the pH sensitivity of the different structures. In each experiment an as-grown and a treated sample were measured simultaneously. For comparison, two types of buffer solutions were used:

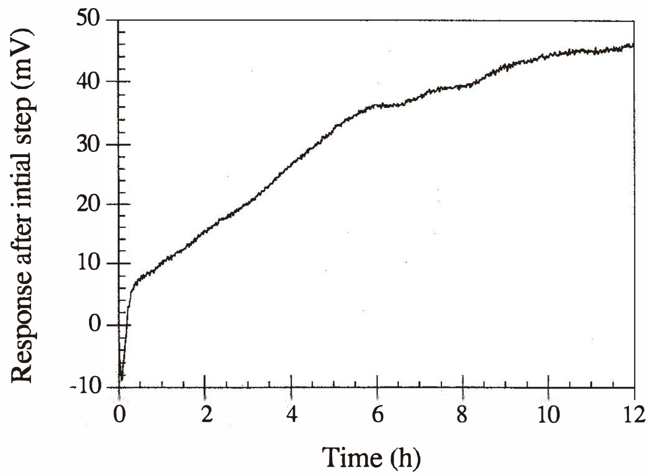
1. TRIS/NaCl : 0.1M TRIS (tris(hydroxymethyl)-aminomethane) and 0.5M NaCl
2. Phosphate/NaCl : 0.01M KH_2PO_4, 0.01M Na_2HPO_4, 0.02M CH_3COOH, 0.02M H_3BO_3 and 0.1M NaCl

The procedure used for measuring drift and hysteresis was adapted from that described by Bousse *et al.*[3] To measure drift, the response of a sample to a pH step from 9 to 7 was measured over a period of 12 h. This also acted as a pre-conditioning step prior to the test. To measure hysteresis the pH was varied in a stepwise approximation of a triangular waveform with steps of approximately one pH unit. The starting pH was 7, after which it was reduced to 4 in three steps, increased to 10 in six steps, and then returned to 7 in three steps. Each step took 10 min, of which 8 min were used to add acid or base to achieve the new value and 2 min were spent measuring the output voltage at a constant pH. The total time for the experiment was 130 min. (This sequence of pH values, pH 7–4–7–10–7, will be herein referred to as a 'pH cycle'.) The pH and voltage values were measured immediately before a pH change along with the final value after the return to pH 7. In a similar manner to that of Bousse *et al.*,[3] a linear regression was carried out on this set of values, yielding an average value of the pH response at the surface and a set of residuals. These residuals were then plotted to show the hysteresis curve. The hysteresis value, H, was taken as the width of the curve at pH 7.

4. Results and Discussion

Typical responses to a pH step are shown in Fig. 1(a) for the as-grown sample and in Fig. 1(b) for the treated sample. Phosphate buffer solution was used in this experiment. After 12 h the drift was approximately 0.4 mV/h for the as-grown sample and 0.04 mV/h for the treated sample. Hysteresis measurements of both samples were taken after this 12

(a)



(b)

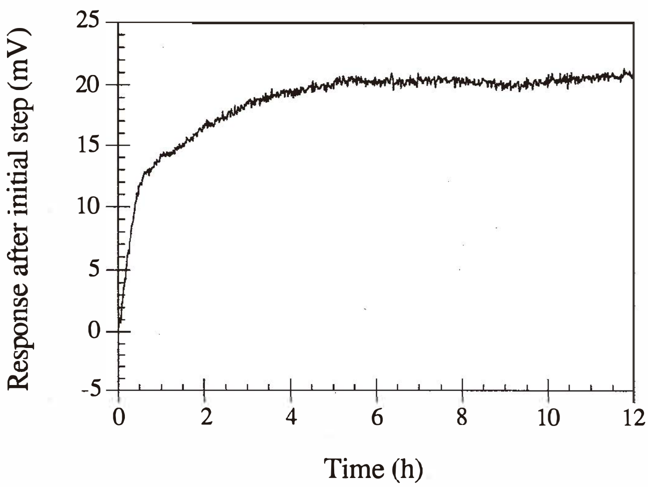


Fig. 1. (a) Response of the as-grown sample to a pH step from 9 to 7. (b) Response of the treated sample to a pH step from 9 to 7.

h conditioning period, thus ensuring that drift would have as little influence as possible on the results. The pH sensitivity for each of these samples is shown in Fig. 2. As can be seen, the pH sensitivity of the treated sample is significantly larger than that of the as-grown sample. From the data in Fig. 2 the hysteresis curves shown in Fig. 3 are calculated. A hysteresis value of 10 mV is obtained for the treated sample and it should also be noted that the hysteresis on the basic side (pH 7–10) is greater than that on the acidic side (pH 4–7).

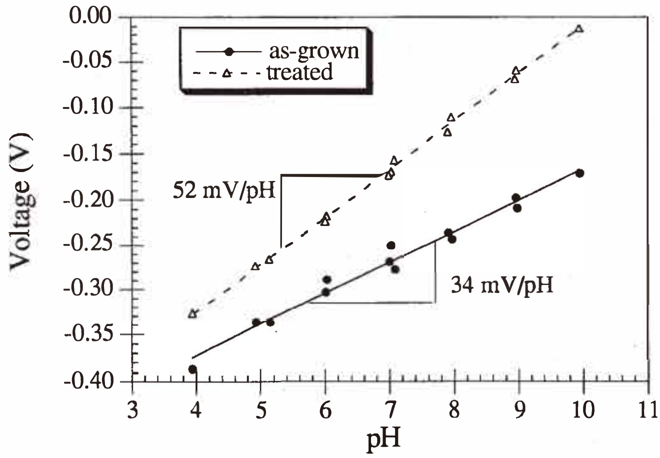


Fig. 2. Typical pH sensitivity characteristics of as-grown and treated samples.

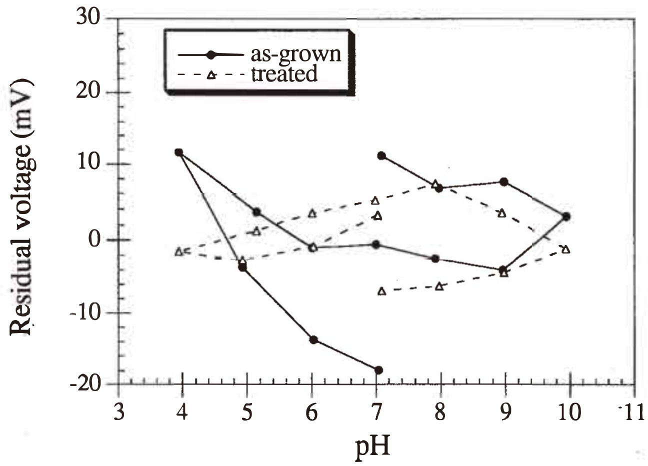


Fig. 3. Typical hysteresis curves for as-grown and treated samples.

These results are in agreement with those reported in the literature.[5] The as-grown sample does not exhibit a standard hysteresis curve, i.e., no hysteresis loop is observed. Instead it appears that the nitride response is drifting towards more positive values. Therefore, this curve cannot be properly described by the parameter H.

In total, eleven samples were used to determine the average drift and hysteresis values for Si_3N_4. Conditioning times of between 12 and 52 h were used. In all cases the as-grown samples exhibited a continuous upward drift with a time response similar to that in Fig. 1(a) while the treated samples tended to approach an equilibrium value with a time response similar to that in Fig. 1(b). Hysteresis measurements were then carried out on each of the samples. From these results the pH sensitivity values of the different samples were obtained and a histogram of these values is depicted in Fig. 4. A much narrower distribution is observed for the treated samples than for the as-grown samples. The mean and standard deviation of the pH sensitivity for the as-grown samples are 34.4 and 3.2 mV/pH, respectively, and those for the treated samples are 51.9 and 1.9 mV/pH, respectively. An increase in mean pH sensitivity of approximately 17 mV/pH is thus obtained for the treated sample. This is larger than the value of 10 mV/pH reported previously.[2] The reason for this is thought to be the influence of hysteresis on the measurement, as will be demonstrated later.

The hysteresis values for the eleven samples are shown in Table 1. Standard hysteresis curves (in the form of a loop) were obtained for all but two of the treated samples. The average hysteresis value is 13 mV and the hysteresis on the basic side is always greater than that on the acidic side. Only two of the as-grown samples exhibited standard hysteresis curves and these occurred when conditioning times of 22 and 52 h were used. The hysteresis values in these cases are significantly larger than those for the treated samples.

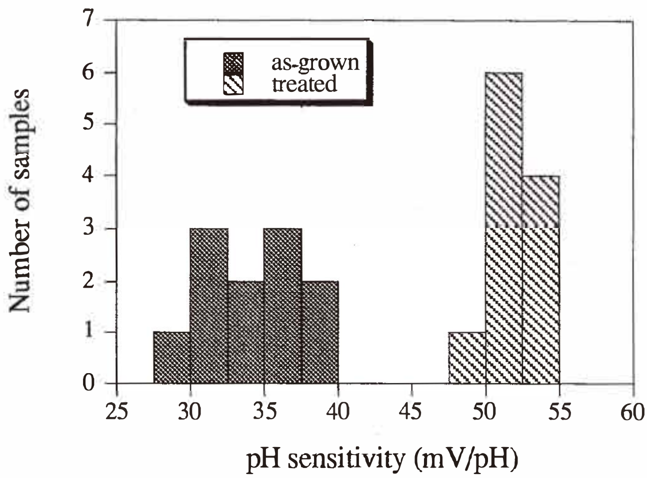


Fig. 4. Histogram of pH sensitivity values obtained for as-grown and treated samples.

Table 1
Hysteresis values for as-grown and treated samples after various conditioning times (i.e., time in pH 7 prior to test).

Time (h)	12	12	14	17	19	22	22	23	36	37	52
H_T (mV)	10	15	ns	ns	7	10	10	12	17	12	18
H_{AS} (mV)	ns	ns	ns	ns	ns	17	ns	ns	ns	ns	24

H_T : Hysteresis value of treated sample
H_{AS} : Hysteresis value of as-grown sample
ns : Non-standard hysteresis curve obtained

Even though the hysteresis value could not be measured accurately for the remaining as-grown samples, it is estimated to be 25–30 mV. This value was obtained by calculating the voltage displacement at pH 7.

A non-standard hysteresis curve was also observed by Bousse *et al.* on Al_2O_3 insulators when NaF was added to the buffer solution.[(3)] It was suggested in this case that extra charge was induced either at the surface or in the bulk of the Al_2O_3 insulator. It was also noted that this apparent drift was irreversible. Considering the two as-grown samples in our study for which a standard hysteresis curve was obtained, hysteresis measurements had also been performed on these samples after conditioning times of 12 and 42 h. After these conditioning times a non-standard hysteresis curve was obtained. A further 10 h in pH 7 solution resulted in these samples exhibiting standard hysteresis curves with hysteresis values of 17 and 24 mV. Therefore, after an increase in conditioning time, a standard hysteresis curve is sometimes obtained for the as-grown samples. According to Bousse *et al.*[(3)] hysteresis is a function of the time response and the amplitude of the slow response of the Si_3N_4 insulator. Further experiments are required to determine the exact relationship for the samples used in this study. However, one significant feature is that the slow response obtained for a treated sample drifts upwards and eventually flattens out as expected. The slow response obtained for the as-grown sample, in contrast, exhibits a continuous upward drift and does not appear to flatten out within the recording interval. Therefore, it is suggested that the standard hysteresis curves obtained for the as-grown samples may be due to an eventual flattening out of the slow response. There does not, however, appear to be any trend in these results relating either the occurrence or value of hysteresis to conditioning time.

To investigate further the effect of hysteresis on the pH sensitivity, samples are measured stepwise from pH 4–10 and compared with those measured using a pH cycle. These samples were not conditioned in solution prior to the hysteresis measurement and were measured in the TRIS buffer. A summary of the results is given in Table 2. The effect of the hysteresis on the pH sensitivity was found to be very small on a nitride surface which has received an RTP treatment. However, the pH sensitivity of an as-grown nitride surface is significantly decreased. As previously mentioned, the non-standard hysteresis curve exhibited by the as-grown nitride surface is due to the response of that surface drifting

Table 2
Comparison of the pH sensitivity of samples measured in solution varied from pH 4–10 with that of samples measured in solution varied in a pH cycle (i.e., pH 7–4–7–10–7). TRIS buffer solution was used. The samples were not stored prior to test.

	pH sensitivity mean and SD of as-grown sample (mV/pH)	pH sensitivity mean and SD of treated sample (mV/pH)
pH 4–10 measurement	39 ± 3.4	53.2 ± 2.7
pH cycle measurement	28.6 ± 4.7	53.8 ± 2.9

towards more positive values. This hysteresis curve has an estimated hysteresis value of 25–30 mV. It is proposed that this continuous upward drift is the major contributory factor to the decrease in pH sensitivity of as-grown nitride.

The effect of different buffer solutions on the pH response was investigated by performing hysteresis measurements in both TRIS and phosphate buffer solutions. This involved conditioning the samples for at least 12 h in a pH 7 solution and then measuring using a pH cycle. A significant difference is observed between the pH sensitivities obtained in the two buffers (Table 3), the mean pH sensitivity being much lower in the TRIS buffer than in the phosphate buffer. It is noted that a similar result has been previously reported.[3] Here the dissimilarity was interpreted in terms of differences in counter-ion adsorption between the two types of solutions.

As discussed earlier, an increase in the amine/silanol ratio results in a shift in pH_{pzc} which in turn results in an increase in the pH sensitivity of the nitride surface. This is a surface effect. It has been suggested that the high drift and hysteresis values of nitride may be due to a bulk effect in the form of buried sites which react slowly to changes in pH.[5] Applying this theory to the RTP treatment, it is proposed that by increasing the amine/silanol ratio and possibly increasing the overall number of amine sites, a higher percentage of sites are more readily available for reaction with the solution. This will reduce the effect

Table 3
Comparison of the pH sensitivity of samples measured in phosphate buffer solution with that measured in TRIS buffer solution. The samples were stored in solution for at least 12 h and measurements were made using a pH cycle.

	pH sensitivitiy mean and SD of as-grown sample (mV/pH)	pH sensitivity mean and SD of treated sample (mV/pH)
Phosphate buffer	33.9 ± 3.4	51.5 ± 1.7
TRIS buffer	28.3 ± 5.5	46.5 ± 4.2

of the buried site reaction and therefore the memory effect it causes. It is not clear whether the improvement in the pH response is due to a surface or a bulk effect, or to a combination of both.

6. Conclusions

During this study the effect of an RTP treatment on a Si_3N_4 surface was investigated, in particular, its effect on the drift and hysteresis of this surface. Our results indicated that RTP-treated surfaces exhibit a lower drift than as-grown surfaces. Treated surfaces also exhibit standard hysteresis curves with an average hysteresis value of 13 mV, while as-grown nitride surfaces typically exhibit a non-standard hysteresis curve with an estimated hysteresis value of approximately twice that of a treated surface. It was also shown that the presence of hysteresis lowers the pH sensitivity of Si_3N_4. Combining these results with the increase in pH sensitivity also observed after an RTP treatment, it is concluded that RTP of a Si_3N_4 surface is a very effective technique for improving the pH response of this surface.

Acknowledgments

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