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Preliminary note

The zeta potential of silicon nitride thin films

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INTRODUCTION

Silicon nitride is used extensively as a pH-sensitive surface in chemical sensors using electrolyte/insulator/silicon (EIS) structures [1–3]. Although many authors report a Nernstian pH response (i.e. near 59 mV/pH, at room temperature), several researchers have found that a treatment in hydrofluoric acid (HF) is needed to obtain such an ideal pH response [2,4,5]. Possible applications of such pH sensors in biological fluids can raise issues of biocompatibility. Because of its excellent properties as an etch mask and a diffusion barrier, and its mechanical hardness, silicon nitride is also commonly used in the micromachining of three-dimensional structures in silicon. The applications of some of these structures involve the interaction of the nitride surface with liquids. Some examples of micromachined silicon structures that can be in contact with liquids are: chambers for the measurement of cell metabolic rates [6], valves [7], tips for atomic force microscopes [8], sieves for fusing individual plant cells [9] and tools for microsurgery [10]. The silicon nitride is most commonly deposited with low-pressure chemical vapor deposition (LPCVD).

In all these applications, it is important to understand the behavior of the charge and potential at the Si_3N_4/electrolyte interface. With EIS structures, it is possible to measure variations of ψ_0, the electrostatic potential difference between the insulator surface and the bulk solution [11,12]. This allows the measurement of the pH dependence of ψ_0. The double layer model most often used to predict the pH dependence of ψ_0 is the surface site model, which can explain most but not all of the observed behavior. In this model, the slope of the ψ_0 vs. pH curve has a minimum at the point of zero charge, both for single-site and two-site surfaces. For Si_3N_4 the model predicts Nernstian behavior provided enough amine sites are present at the surface [2], and this is indeed what is observed [2,3]. Such a linear

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potential/pH relationship makes it impossible to determine the point of zero charge of silicon nitride by locating the pH where $d\psi_0/dpH$ is a minimum.

However, as will be shown below, in order to understand the surface chemistry of Si_3N_4 it is important to know its point of zero charge, pH_{pzc}. This can be determined with a zeta potential measurement [13]. Previous work [14] using electrophoresis on a silicon nitride powder found pH_{pzc} to be in the range of pH 2 to 4, which is not very different from SiO_2. This suggests that the surface of silicon nitride is practically the same as that of SiO_2, and that virtually no ionizable amine groups remain at the surface. This measurement, however, was done on a powder of α-phase silicon nitride, as opposed to the amorphous thin films deposited by LPCVD. It was therefore desirable to carry out the electrokinetic measurements on th same LPCVD-deposited material as is used in the applications mentioned above. Here we report measurements obtained by the flat-plate streaming potential method described by Van Wagenen et al. [15] of the zeta-potential and the point of zero charge of thin films of LPCVD-deposited Si_3N_4.

MODEL OF THE SILICON NITRIDE SURFACE

Harame et al. [2] have proposed that the surface of silicon nitride is composed of both Si–OH (silanol) sites and primary amine sites $Si–NH_2$. This model of the surface is supported by surface analysis methods which indicate that both oxygen and nitrogen are present at the surface [16,17]. The primary amine sites $Si–NH_2$ are expected to have a pK of around 10. Since the point of zero charge of silicon nitride always has a value much lower than 10, it can be assumed that all the amine sites are positively charged at the point of zero charge. Thus, at most pH values, the silanol sites tend to donate a proton to the amine sites. The point of zero charge occurs at the pH where the negative charge on the silanol sites balances the fixed positive charge on the amine sites. This is shifted upwards from the pH_{pzc} of the silanol sites alone. The surface site theory [2,12] can be used to calculate the relationship between the shift in the point of the charge, and the ratio of the number of amine sites to silanol sites on the surface:

$$\frac{N^{NH_2}}{N^{OH}} = 2\sqrt{\frac{K_{a2}}{K_{\alpha 1}}}\ \sinh\left[2.303\left(pH_{pzc} - pH_{pzc}^{OH}\right)\right] \tag{1}$$

in which K_{a1} and K_{a2} are the surface equilibrium constants of the two acid/base reactions of the amphoteric silanol sites, and pH_{pzc}^{OH} is the point of zero charge of the silanol sites only. From ref. 11 we obtain the numerical values $pH_{pzc}^{OH} = (pK_{a1} + K_{a2})/2 = 2.2$, and $2(k_{a2}/K_{a1})^{1/2} = 7 \times 10^{-4}$. We will neglect here any differences between the point of zero charge and the isoelectric point. Such differences can occur if there is strong specific adsorption of anions or cations. The term pH_{pzc} will be used to refer to the pH where both the zeta potential, and surface charge are zero; this occurs at the same pH value in the absence of strong specific adsorption [13,18,19].

EXPERIMENTAL

The silicon nitride was deposited on 100 mm diameter silicon wafers by the reaction of ammonia with dichlorosilane, at 800 °C and 350 mTorr. The film thickness was about 100 nm, as measured by ellipsometry. The wafers were diced into four rectangular strips of 80 by 12.5 mm, which were then mounted in the sample holders shown in Fig. 1. These sample holders are different from those reported by Van Wagenen et al. [15] in that the edges of the samples are not exposed to solution. This is important for this application where an insulating film is deposited on a conducting substrate.

The dimensions of the flow channel were measured to be 68 mm by 10 mm by 75 μm. The rest of the measurement setup was generally similar to that described in ref. 15; two vessels were used and measurements of pressure and potential were differential between them. Pressure was applied as an alternating square wave with a four-minute period. The streaming potential was found as the slope of the potential changes vs. pressure changes when the pressure is switched between vessels. The flow resistance was measured to calculate average velocities and Reynolds numbers. At the highest pressure used (1 bar), the Reynolds number was 52, which means that flow was always in the laminar region. These data were also used to verify that the corrections for short capillaries calculated by Bowen [20] were negligible. After each measurement, the pH and conductivity of the electrolyte solution were measured. The zeta potential is calculated from the streaming potential with the Helmholtz–Smoluchowski equation.

All experiments on silicon nitride were done in 0.01 M NaCl, with added buffers at low concentration to provide pH stability. NaCl solutions were chosen because their composition is similar to physiological saline encountered in biological applications. The pH range covered was 6.2 to 2.4.

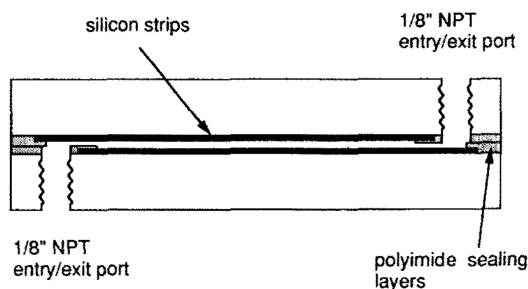

Fig. 1. Cross-sectional diagram of the sample holders, which are machined from a polycarbonate plastic. 1″ ≈ 25.4 mm.

RESULTS

An example of a zeta potential vs. pH curve is shown in Fig. 2. From such a data set, pH_{pzc} can be deduced by interpolation. We have found that this point of zero charge depends on time, on the history of the sample, and on the exposure to HF.

Data of time evolution of pH_{pzc} for two samples is shown in Fig. 3. Sample 1 was a silicon nitride surface which had been exposed to air for several years prior to measurement. At its first exposure to solution, pH_{pzc} was very low (around pH 2). This is what is expected of SiO_2, indicating that in the course of time this surface became entirely oxidized. Then the surface oxide was removed with a solution of 1% HF for 2 min. As expected, after the HF etch the point of zero charge of the surface went up, but only to about 3.9. This is the highest value we have seen for a nitride surface; eqn. (1) can be used to calculate that this corresponds to the presence of 1.8% amine sites and 98.2% silanol sites. After the HF etch, the pH_{pzc} declines slowly with further exposure to the electrolyte solution, and then appears to stabilize at pH 3.5, where the number of amine sites is about 0.7% of the total. Sample 2 was younger (nitride deposition occurred about six months before the experiment), and started out at a higher pH_{pzc}. This sample was not etched in HF immediately, but was hydrated for a certain period in the 0.01 M NaCl measurement solution.

The results of Fig. 3 can be summarized as follows: both hydration in solution and HF etching of the surface oxide increase pH_{pzc}. In the case of hydration, the increase is slow, and it takes about a week for pH_{pzc} to reach pH 3.7. HF etching

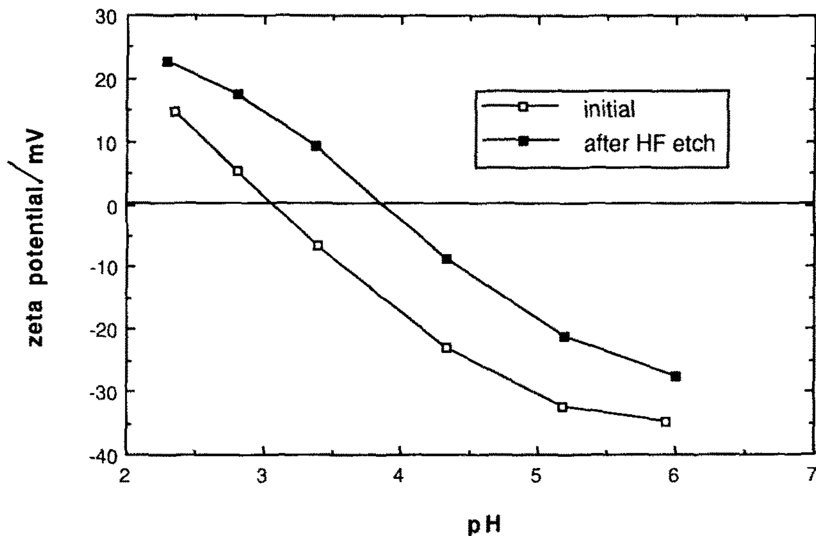

Fig. 2. Zeta potential of silicon nitride (sample 2), after first exposure to the 0.01 M NaCl solution, and after a 2 min exposure to 1% HF.

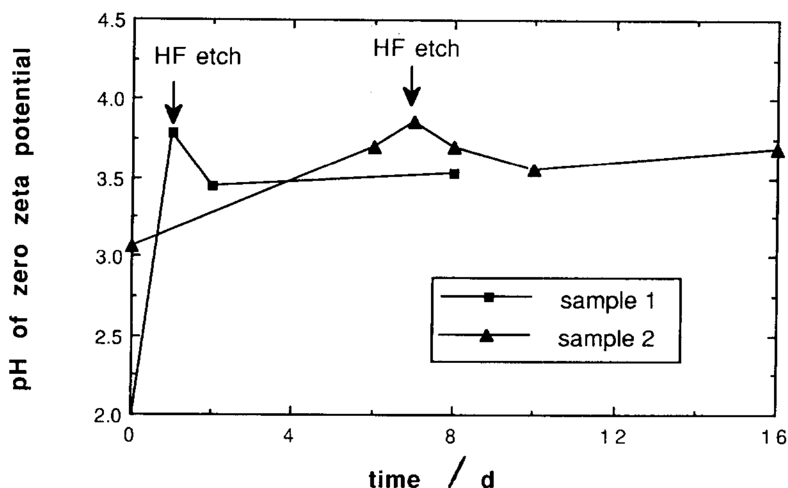

Fig. 3. Evolution of the point of zero zeta potential of two samples as a function of time and treatment with a 1% HF solution.

causes the point of zero charge to go up immediately to 3.9, after which it declines slightly, and appears to stabilize at 3.5. The number of amine groups present at the surface never exceeds 2% of the total, which means the surface is always very close to a pure silanol surface. At the steady state reached after long exposures to a liquid, there are about 1% amine groups on the surface.

DISCUSSION AND CONCLUSIONS

These results generally agree with those obtained by electrophoresis on a silicon nitride powder [14]. The main difference is that the powders appeared to oxidize more readily, and their point of zero charge declined to below pH 3 after long exposures to solution. Our result that some amine sites appear to remain indefinitely on the surface is of importance in explaining why the pH response of LPCVD-deposited Si_3N_4 does not degrade with time. The theory of ref. 2 predicts that only a small number of amine sites is needed to ensure a Nernstian response. Nitrides made by other methods may be more susceptible to oxidation, which is expected to make their pH response poorer. For properties such as biocompatibility or protein adsorption, which depend on the global chemical nature of the surface, Si_3N_4 is expected to be very similar to SiO_2.

We are continuing work on investigating the silicon nitride surface by the means of streaming potential measurements. In particular, we will explore ionic strengths different from the 0.01 M used here, and the effect of treatments with strong acids and bases on the point of zero charge.

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