PECVD SiO$_2$/Si$_3$N$_4$ Double-layer Electrets for Application in Micro-devices

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Abstract. In this paper, the influence of different environmental conditions, substrates, micromachining processes, areas and patternings on the performances of PECVD SiO$_2$/Si$_3$N$_4$ double-layer electrets were studied for its application in micro-devices. Various samples were prepared and then charged by the negatively corona charging method. The charge decays at either 250°C or 95%RH were observed to reveal the chargeability and charge stability. Finally, a micro power generator with patterned PECVD SiO$_2$/Si$_3$N$_4$ double-layer electret was presented briefly as demonstration. The results show that all these conditions that conventionally or even unavoidably happen in the fabrication process of electret micro-devices had more or less impact on the electret performance. It is crucial that the electret should be as large area as possible and kept from the micromachining processes and humid condition to the best. Our micro power generator with 2mm rectangular array of PECVD SiO$_2$/Si$_3$N$_4$ double-layer electret had the 5.9µW output power at 20Hz and 0.7g.

1. Introduction
Due to its stable charge storage and other useful properties, electrets have been widely applied in electric-acoustic transducers [1], electret filters [2], electret dosimeters [3], and etc.. Silicon-based inorganic electrets, such as SiO$_2$, Si$_3$N$_4$ and SiO$_2$/Si$_3$N$_4$ double–layer, have been well studied [4-6] for their high charge stability and compatibility to IC and micromachining technologies. Especially, it was proved that the SiO$_2$/Si$_3$N$_4$ double–layer electrets had better performance than other two single layer ones [7]. SiO$_2$/Si$_3$N$_4$ double layers are prepared traditionally by thermal oxidation or APCVD/LPCVD on silicon substrates. Compared to these high temperature deposition methods, PECVD has the advantages of relatively high deposition speed, low temperature, low residual stress and compatibility with both silicon and non-silicon substrates. Our primary experimental results had proved the good chargeability and stable charge storage of PECVD SiO$_2$/Si$_3$N$_4$ double–layer electrets on glass substrates [8-10]. However, when the electret is utilized in micro-devices its area is much smaller than that in material property research and it even has to be patterned such as rectangle array, which may influence its performance significantly. Additionally, the electret must go through various micromachining processes inevitably for the micro-device fabrication. In this paper, we mainly investigate the influence of different substrates, micromachining processes, areas and patterning on the performance of PECVD SiO$_2$/Si$_3$N$_4$ double-layer electrets. Finally, a micro power generator with patterned this kind of electret was presented briefly as demonstration.

2. Samples Preparation
4-inch Pyrex-7740 glass wafers were used as substrates. Only the sample for comparison of different...
substrate materials was prepared on silicon substrate. Cr/Au (30nm/100nm) as lower electrode were sputtered at first. Then, 1μm SiO2 and 50nm Si3N4 were deposited by PECVD in turn. For all samples, SiO2 was deposited at a speed of 120nm/min, and Si3N4 at a speed of about 15nm/min at 300°C (substrate temperature). Finally, Al (500nm) as back electrode was sputtered on the back of the substrates to form a good contact with ground. All these wafers were cut into 3cm×3cm pieces as samples except for those for studying on the effect of different areas and patterning on the electret performance. Samples of different areas are 1cm×1cm, 2cm×2cm, 3cm×3cm and the whole 4inch wafer. The rectangle arrays of electret are made of same width and gap of periodic stripes, including 1mm, 500μm, 200μm, and 50μm, on 1cm×1cm substrate.

Table 1. Different conventional micromachining processing conditions.

| Process                          | Condition                  |
|----------------------------------|----------------------------|
| Oxygen plasma stripping          | 10min                      |
| Stripping with acetone           | 10min                      |
| Fuming nitric acid stripping     | 15min                      |
| H2SO4 and H2O2                   | 100°C, 30min               |
| H3PO4, HAc and HNO3              | 39°C, 30min                |
| I2 and KI                        | 33°C, 30min                |

The micromachining process for the electret patterning can be mainly divided into two groups: (1) photolithography with different photo-resistor (PR) stripping processes, such as oxygen plasma, acetone and fuming nitric acid; (2) conventional cleaning or wet etching processes, including H2SO4 and H2O2 (common cleaning liquid), corrosive of Au (I2 and KI) and corrosive of Al (H3PO4, HAc and HNO3). The processing conditions are listed in table 1. After wet processing, all samples were flushed by DI water and then dried by nitrogen gas.

Before charging, all samples were ultrasonically cleaned and dehydrated at 150°C for one hour. Then, they were stored in silica gel desiccators at room temperature to be insulated from moisture and contaminants in outside. These samples were negatively corona charged at 80°C for 30min with only the back electrode grounded. The tip voltage is -5kV, and the grid voltage is -400V. The distance between the tip and sample surface is about 15mm, and the grid is 2mm above the sample.

3. Measurement Methods
The Surface potential was measured by Trek 347 voltmeter with TRE-6000B-7C probe. Five points of every sample were measured and the average surface potential was calculated. The absolute value of the surface potential was adopted in all figures and context of this paper for convenience. The average surface potential after 30min heat treatment (V30min) at 250°C was used as initial surface potential. Then, all samples went through 250°C heat-treatment for 300min in the oven and the surface potential was measured every 30min (Vt) except for the long-time-observation samples. The normalized data were obtained by Vt/V30min for comparing the charge stability of different samples. At last, High humidity charge decay was operated at 95%RH, 25°C and surface potential was measured every 30min for all samples except the long-time-observation sample. According to our previous research [8], the performance of PECVD SiO2/Si3N4 double-layer electrets in high humidity condition can be improved by heat treatment significantly. Therefore, all the samples were heat treated at 250°C for 3hr before high humidity charge decaying. And so the normalized data were obtained by Vt/V3hr.

4. Results and Discussions

4.1. Surface Potential during Long Time Observation
The surface potential of samples charged at typical conditions was observed at room temperature for 38 days and measured once several days (figure 1). They were kept in three kinds of circumstances of: (I) silica gel desiccators except measuring time; (II) outside; (III) outside after 250°C 3hr heat treatment.

After 38 days, samples of (I), (II) and (III) still had 89%, 61.5% and 95.5% of their initial surface
potential, respectively. The surface potentials of both samples (I) and (III) descended slowly and linearly, but that of sample (II) decreased rapidly at first 5 days and then the trend slowed down and became linear. Sample (II) has the highest drop in initial surface potential up to 40V/day, revealing that ions and water molecules in outside can impair the charge stability effectively. After several days, its dropping velocity decreased and kept about 1.3V/day. Although the surface potential of sample (III) dropped just 0.3V/day much slower than 1V/day of sample (I), sample (III) paid more than 150V surface potential decreasing during 250°C 3hr heat treatment as cost. Sample (II) always shows fastest charge losing than others and even lower surface potential than sample (III) after one month. Therefore, if the PECVD SiO2/Si3N4 electret has to work outside proper heat treatment must be done.

Figure 1. Normalized charge decay of three samples kept in different environmental conditions (inset is charge decay curve).

4.2. Influence of Different Substrates
The silicon and glass are two main kinds of substrates in micro-devices. Figure 2 exhibits that PECVD SiO2/Si3N4 double-layer electret on glass has the similar charge stability at high temperature and humidity with that on silicon and even a little better chargeability (inset of figure 2(a)). It indicates that substrate has no impact on the performance of PECVD SiO2/Si3N4 double-layer electret.

Figure 2. Normalized charge decay of PECVD SiO2/Si3N4 double-layer electret prepared on silicon and glass substrates: (a) at 250°C (inset is charge decay curve); (b) at 95%RH.
4.3. Influence of Different Micromachining Processes

Figure 3 shows the charge decay curves of samples processed by different PR striping techniques and that of unprocessed one. Initial surface potentials (V30) of processed samples were much lower than unprocessed one (inset of figure 3(a)), indicating that these PR striping processes decrease the chargeability of SiO$_2$/Si$_3$N$_4$ double-layer electret. Although they have no reaction with SiO$_2$/Si$_3$N$_4$, acetone and fuming nitric acid may impact on the surface state resulting in the trapped charge decreasing. Whether in bulk or on the surface, it is well known that ions can depress the performance of electret seriously. The fuming nitric acid processing made the surface potential decrease much more than the acetone, because it is unavoidable that the water in air or attached on the sample surface was absorbed and ionized somewhat. As can be seen from the figure, samples processed by acetone and fuming nitric acid have similar charge stability at high temperature and humidity with unprocessed samples. Whereas, both the surface potential and the charge stability were decreased significantly by the oxygen plasma stripping processing. The reason may be that the oxygen ion can bombard the sample surface for over-etching and possibly left as recombination defects.

Figure 3. Normalized charge decay of samples processed by photolithography with different stripping techniques: (a) at 250°C (inset is charge decay curve); (b) at 95%RH.

Figure 4 shows the charge decay curves of samples processed by conventional cleaning or wet etching processes and that of unprocessed one. It can be seen that all of these processes decrease the chargeability of SiO$_2$/Si$_3$N$_4$ double-layer electret (inset of figure 4(a)). And all these samples also have similar charge stability at high temperature and humidity with unprocessed samples. This phenomenon may be explained by above analysis about fuming nitric acid with which these solutions would have similar impact on the SiO$_2$/Si$_3$N$_4$ double-layer electret.

Figure 4. Normalized charge decay of samples processed by various etching techniques: (a) at 250°C (inset is charge decay curve); (b) at 95%RH.
4.4. Influence of Different Areas and Patterning

4.4.1. Different Areas. It can be seen that the chargeability decreasing with the decreasing area with the order of 4inch wafer (diameter=10cm) the largest of initial surface potential ($V_{30}$), 3cm×3cm and 2cm×2cm samples the smaller, and 1cm×1cm sample the smallest (inset of figure 5(a)). This phenomenon of may result from the ratio of edge to area. There are three major routes of charge decay: surface, edge and bulk. The closer to the edge of the sample, the easier the charge vanishes. Small area sample has large ratio of edge to area and its charge decays seriously. All four samples exhibit similar normalized charge decay, revealing that there is no floating charge after 30min isothermal charge decaying. And they all kept higher than 95% initial surface potential after 5hr at 95%RH (as shown in figure 5 (b)) indicating that they have high stability in high humid condition. Therefore, decreasing the sample area can depress the chargeability but has no impact on the charge stability.

![Figure 5](image-url)

**Figure 5.** Normalized isothermal charge decay of samples with different areas: (a) at 250°C (inset is charge decay curve); (b) at 95%RH.

4.4.2. Patterning. The surfaces potentials of the samples with rectangular arrays are much lower than that of without one (i.e. the whole 1cm×1cm electret) (inset of figure 6(a)). The chargeability decrease may result from two aspects. One is that patterning largely increases the ratio of edge to area as discussed above. The other is that the total area of these rectangular array samples is just half of the whole 1cm×1cm one. If the chargeability is same and the charge distributes symmetrically, the total charge and surface potential in any of these samples should be half of that of the whole 1cm×1cm one at best. The sample with 1mm width of rectangular bar did show the surface potential about half of the
whole 1cm×1cm one, revealing that they have same chargeability. Whereas, the surface potential of other samples are lower than the half of that of the whole 1cm×1cm one and decrease significantly with the reducing width of rectangular bar. The sample with 50μm width bar only has about 30V surface potential. It can be deduced that the chargeability shows a significant reduction when the width of rectangular bar is smaller than 1mm. Most samples almost have similar charge stability at 250°C except the sample with 50μm width bar which is significantly lower than others (as shown in figure 6(a)). The charge stability at high humidity of the whole 1cm×1cm sample is almost same with that of 1mm width bar one. However, the charge stability at 95%RH decrease obviously with the decreasing rectangular bar width (as shown in figure 6(b)). Both the chargeability and charge stability were impacted by rectangular bar width although the total area is the same, which is conflicted with the results of figure 6. And the narrower the rectangular bar is the more serious this phenomenon is. This is because that the ratio of edge and area increases with the decreasing of the rectangular bar width. The edge area contains much more defects than the bulk and also play the role like the surface. And it must be considered that the edge of patterned samples had to directly experience RIE and BHF wet-etching techniques to obtaining the rectangular shapes with different widths. These etching processes made the edge area suffered and augmented the defects furthermore.

4.5. Micro Power Generator with Patterned Electret

A micro power generator for vibration energy harvesting from the environment using patterned PECVD SiO₂/Si₃N₄ double-layer as electret was proposed by us [11]. The device was fabricated by simple micromachining technology suitable for batch production. According to above results, the electrets was patterned as strips with a width of 2mm and a length of 27mm. When the oscillation frequency and acceleration are respectively set to 20Hz and 0.7g and the external load resistance is 626kΩ the peak-to-peak charge output of micro power generator is 72nC and the power output is 5.9µW, illustrating that the vibration energy was successfully harvested and transformed to electricity energy by our device.

5. Conclusion

In this paper, we mainly study on the influence of different environmental conditions, substrates, micromachining processes, areas and patternings on the performances of the PECVD SiO₂/Si₃N₄ double-layer electret for its application in micro-devices. Long-term observation implies that hermetic packaging is the best option, and if the electret has to work outside proper heat treatment is necessary. Different substrates have no obvious impact on the performance of electret. Wet processes having no reaction with SiO₂/Si₃N₄ double-layer can make the chargeability decrease significantly but not the charge stability. However, both the chargeability and charge stability can be depressed by oxygen plasma stripping. Decreasing the area of sample can depress the chargeability but has no impact on the charge stability. Both the chargeability and charge stability decreases with the decreasing width of rectangular bar when rectangular bar is narrower than 1mm because of the ratio of edge and area increasing and suffering from the patterning processes of RIE and BHF wet-etching techniques on the edge. A micro power generator with 2mm rectangular array using PECVD SiO₂/Si₃N₄ double-layer electret has the 5.9µW output power at 20Hz and 0.7g.

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