

A Novel Technology for Post-Treating of Porous Silicon Thick Films in H₂O₂*

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Abstract: The solution of H₂O₂ is proposed to post-treat thick porous silicon (PS) films. The prepared PS film as the cathode is applied about 10mA/cm² current in mixture of ethanol, HF, and H₂O₂ solutions, which is expected to improve the stability and the smoothness of the surface and the mechanical property of the thick porous silicon films. The microstructure of the PS thick films with thicknesses of 20μm and 70μm has been studied. The SEM images show significant improved smoothness on surface of PS films, and XRD spectra suggest the formation of oxide layer after post-treating in H₂O₂.

Key words: porous silicon; post-treatment; H₂O₂

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1 Introduction

Since the photoluminescence properties^[1] of porous silicon (PS) were discovered in 1990, porous silicon has been applied in many fields. During the last decade porous silicon has been a widely studied material due to special properties of porous silicon and its possible applications, such as light emitting devices, sensors, biomedical applications, micro-machining devices as the sacrificial layer in radio frequency (RF)/microwave circuits^[2] and a thick film as a low-loss or high resistivity interlay-

er^[3] for passive elements in the monolithic microwave integrated circuit. However, porous silicon, especially, that with high porosities and thick porous silicon films is very unstable in the air. After the formation of a high porous or thick PS films, when the electrolyte and hydrogen evaporate out of the pores in the air, a cracking of the layer occurred. It excessively restricts the applications of porous silicon.

Many methods or technologies such as pentane drying, supercritical drying, freeze drying and slow-evaporation rates have been proposed to post-treat porous silicon films to reduce or eliminate the

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capillary stress. Pentane drying is the easiest method to implement. Pentane has a very low surface tension, and shows no chemical interaction with PS. All the above methods or technologies let the electrolyte and the hydrogen evaporate out of the pores of porous silicon films. Because the surface of porous silicon films is very fragile, a cracking of the layer is usually formed.

In this paper, a novel, effective and simple technology for post-treating of thick porous silicon films is proposed. H_2O_2 is used to post-treat the surface of porous silicon to reduce Si—H bonds in the internal surface of porous silicon, and make the surface of porous silicon films to form a layer of porous SiO_2 . The experimental results show that the method can enhance the stability and the smoothness of the surface and the mechanical intensity of the thick porous silicon films in the air.

2 Experiment

After the formation of porous silicon, the internal surface of the PS films is very large. The ratio^[4] of the surface area over the volume is as high as $1000m^2/cm^3$. Such a large surface contains an enormous quantity of impurities coming from the electrolyte used for electrochemical etching and from the ambient air. The main original impurity what is always found in PS films is hydrogen. Infrared absorption (IR) experiments have shown the presence of Si—H_x groups ($x = 1, 2, 3$) on the internal PS surface during the etching process^[5]. In freshly porous silicon samples, there are a lot of Si—H bonds in the internal surface of porous silicon, the atomic ratio^[4] H/Si in PS is as high as 0.1 ~ 0.6, depending on the porosity and surface area of the samples. This result means that the surface of freshly etched porous silicon is almost totally covered by Si—H_x groups. Si—H_x groups are unstable in the air, and hydrogen will be released, resulting in an unstable surface of porous silicon.

After the formation of porous silicon, a gas/liquid interface forms inside the pores and a pres-

sure drop^[6] Δp occurs, during evaporation, which is given by

$$\Delta p = \gamma \frac{S \cos \theta}{P}$$

where γ is the liquid surface tension, S the interface area, $\cos \theta$ the curvature of the gas/liquid interface, and P is the porosity. Δp is as high as some MPa.

In order to reduce Si—H_x groups, we propose that the Si—H bonds are progressively replaced by Si—O bonds through reaction with H_2O_2 in mixture of ethanol, HF (47%) and H_2O_2 solutions after the formation of porous silicon.

The chemical reaction in the electrolyte can be described.

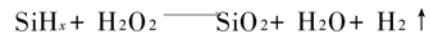


Figure 1 shows the schematic diagram that H_2O_2 attacks the Si—H bonds. After the chemical reaction, the Si—H bonds are replaced by the Si—O bonds. When drying porous silicon films with post-treatment in H_2O_2 , there are not nearly Si—H bonds in the internal surface of porous silicon. During the evaporation, there is not almost hydrogen. A gas/liquid interface forms inside the pores and a pressure drop Δp is very small. Meanwhile, the surface of porous silicon films is protected by the porous SiO_2 . Therefore, there is not a cracking of the layer on the surface of porous silicon films.

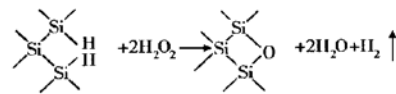


Fig. 1 Schematic diagram of H_2O_2 attacking Si—H bonds

Experimentally, porous silicon was traditionally prepared by anodic electro-chemical etching. The silicon sample and platinum electrode were immersed in an electrolyte which is commonly a mixture of ethanol and HF (47%) (a typical volume ratio is 1 : 1). PS samples were produced by anodization of (100) P-type silicon wafers with $0.01\Omega \cdot cm$ resistivity with a current density of $20mA/cm^2$ in darkness for 21 and 75min, respec-

tively. Thicknesses of porous silicon films were about $20\mu\text{m}$ and $70\mu\text{m}$, respectively.

After the formation of porous silicon, the porous silicon sample acts as the cathode while the anode was platinum. The porous silicon sample as the cathode was applied about $10\text{mA}/\text{cm}^2$ current in mixture of ethanol (100%), HF (47%) and H_2O_2 solutions (a typical volume ratio was 10 : 10 : 1, respectively) for about 5min. Hydrogen in the cathode will be taken off. At last the porous silicon sample was put into 1% H_2O_2 to clean for about 20min. Experimental results show that the micro-structure of PS films depends on the volume ratio of $\text{H}_2\text{O}_2/\text{HF}$ solution and the time of post-treatment.

3 Results and discussion

In order to evaluate the improved performance by post-treating porous silicon films using H_2O_2 solutions, four porous silicon samples with thicknesses of $20\mu\text{m}$ and $70\mu\text{m}$ were prepared. Two porous silicon samples directly dried in the air after the formation of porous silicon films and the other were post-treated in H_2O_2 solutions. Figures 2 and 3 show the SEM images on surface of different porous silicon films. Figures 4 and 5 show XRD spectra of thick porous silicon films.

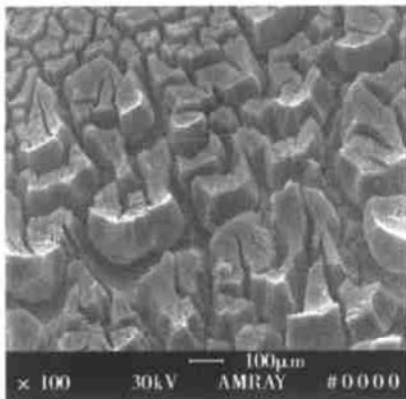


Fig. 2 SEM image of PS(thickness of $70\mu\text{m}$) surface without post-treatment (about 67% porosity)

Figure 2 shows a typical example of cracking pattern without any post-treatment. When the elec-

trolyte and hydrogen evaporate out of the pores, the surface of porous silicon will crack. A cracking of the layer is systematically observed. Inter-distance of cracking was about $1\sim 100\mu\text{m}$.

Figure 3 shows SEM images of porous silicon with post-treatment in H_2O_2 solutions. After post-treatment, the Si-H_x groups almost do not present on the inner surface of porous silicon, and the surface is protected by the porous SiO_2 layer. When the electrolyte evaporates out of the pores, the surface of porous silicon will not crack, the micro inter-distance is about 20nm on surface of the porous silicon films.

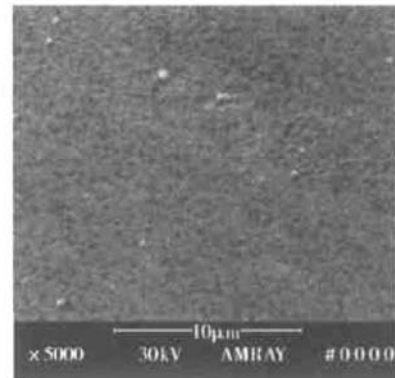


Fig. 3 SEM image of PS(thickness of $70\mu\text{m}$) surface with H_2O_2 post-treatment (about 67% porosity)

Figure 4 shows that XRD spectra of P(100) silicon wafer, PS without any post-treatment and with post-treating in H_2O_2 . XRD spectra of the P(100)-type silicon ($0.01\Omega\cdot\text{cm}$) wafer in Fig. 4(a) shows a very narrow width and a very sharp peak at 68.783° , which shows the nature of the silicon wafer. XRD spectra are distinct variations between the PS surface without any post-treatment and with post-treatment in H_2O_2 . The PS without any post-treatment shows a broadened small peak at 68.781° . The lattice parameter expansion $\Delta\alpha/\alpha$ is about 2.55×10^{-5} . The origin of this expansion^[7] is related to the silicon-hydrogen bonds at the inner surface of the PS films. A very sharp peak in Fig. 4(c) at 68.874° shows the PS characteristic with post-treatment in H_2O_2 , and the lattice parameter contraction $\Delta\alpha/\alpha$ is about 1.27×10^{-5} . What the

formation of oxide layer displaces the Si—H bonds originates a contraction of $\Delta\alpha/\alpha$ (3.82×10^{-5}) due to post-treatment. Moreover, this peak becomes very narrow as shown in Fig. 4(c), which confirms the formation of pores on the surface of porous silicon and there are few Si—H_x groups in the internal surface of PS films. The crystallite size of PS with post-treatment in H₂O₂, which is the representation of the remnant silicon portion after the post-treatment and formation of pores become smaller than which of PS without any post-treatment.

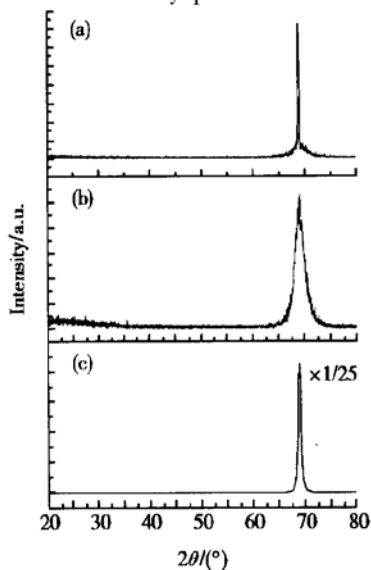


Fig. 4 XRD spectra of P(100) silicon ($0.01\Omega \cdot \text{cm}$) wafer (a), PS with thickness of $20\mu\text{m}$ without post-treatment (b) and with post-treating in H₂O₂(c)

In Fig. 5 a small peak at 32.62° was observed and the lattice parameter (a) equals 0.272nm , which is the consequence of the formation of SiO₂ (110β) films after post-treating in H₂O₂. The result demonstrates the formation of oxide films due to post-treating in H₂O₂. Further, the presence of this peak^[5] in the PS structures confirms that the cubic structure of the PS is retained after post-treatment.

4 Conclusion

We have presented the solution of H₂O₂ to post-treat thick porous silicon films (thickness is

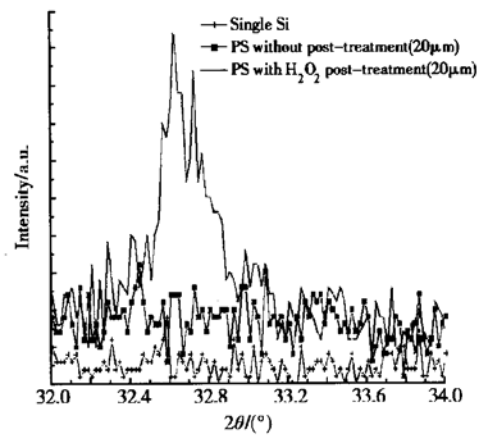


Fig. 5 XRD spectra of different wafers at small 2θ

about $70\mu\text{m}$), the micro inter-distance of porous silicon is about 20nm on the surface of the porous silicon films. The SEM image shows significant improved smoothness on surface of porous silicon films after post-treating in H₂O₂. XRD spectra reveals the formation of oxide films after post-treating PS in H₂O₂. This treatment will also enhance the stability, the smoothness and the mechanical intensity of the thick porous silicon films.

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用过氧化氢后处理多孔硅厚膜的一种新技术*

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摘要: 提出使用过氧化氢后处理多孔硅厚膜. 在乙醇、氢氟酸、过氧化氢溶液中, 多孔硅样片做阴极施加电流密度为 $10\text{mA}/\text{cm}^2$, 希望通过后处理增强多孔硅表面的稳定性、光滑度和机械强度. 研究了厚度为 $20\mu\text{m}$ 和 $70\mu\text{m}$ 的多孔硅厚膜经过过氧化氢处理后的微结构. 扫描电镜图显示经过过氧化氢处理后的多孔硅厚膜表面的光滑度有极大的提高, X 光衍射光谱揭示经过过氧化氢后处理后多孔硅表面形成了一层氧化膜.

关键词: 多孔硅; 后处理; 过氧化氢

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