

Pulse Current Electrochemical Deposition of Silicon for Porous Silicon Capping to Improve Hardness and Stability

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This paper presents a method to improve the stability of porous silicon structures by electrochemical deposition of silicon capping. Porous silicon is formed by pulse electrochemical etching, followed by pulsed current electrochemical deposition, to provide a uniform silicon capping layer on the porous structure. The capping layer thickness and hardness increase with deposition time. The variation of strain in the porous structure is also observed with varying silicon capping layer thickness. Silicon capping of 4 μ m was sufficient to protect porous silicon from aging effects on their spontaneous emission, while a capping of 7.2 μ m causes a 40 nm redshift on the spectrum.

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Manuscript submitted September 19, 2008; revised manuscript received November 12, 2008. Published December 23, 2008.

Porous silicon (PS) has been demonstrated to be a promising material for visible light emission both by electroluminescence and photoluminescence (PL).^{1,2} Most of the investigations have been primarily concerned with the optical properties of PS. However, for device fabrication purposes, information concerning the mechanical properties of PS is also required. The use of PS has several drawbacks, determined by its brittleness and by the instability connected to the aging process, i.e., the slow spontaneous oxidation of PS. Due to the aging effect, the structural' and optical properties⁴ of PS show continuous change with the storage time. The growth of the native oxide is completed after approximately 1 year.⁵ Various oxidation approaches, such as chemical oxidation,⁶ anodic oxidation,⁷ conventional furnace oxidation,⁸ rapid thermal oxidation,⁹ and aging oxidation,¹⁰ were used to generate a more stable O-passivated surface to replace the unstable H-passivated surface to eliminate the aging problem. The high-temperature treatment necessary for the formation of a high-quality silicon/SiO₂ interface leads to a very rapid oxidation rate, which may produce an unacceptably large oxide thickness or even the full conversion of PS into a porous glass.

However, PS has other disadvantages: mechanical instability due to the high porosity and the difficulty of integration of the electrochemical etching needed to produce PS with the Si very large scale integrated processing technology. A proposed solution to solve the problem of the mechanical stability of the porous layer has been the use of multilayered structures in which the high-porosity active layer is sandwiched between two low-porosity supporting layers. This structure shows also improved luminescence stability but a lower intensity.¹² Morales-Masis et al.¹³ have studied the relation between porous layer thickness and its hardness. A slight decrement in the Vickers hardness was observed with increasing porous layer thickness. Recently, the experimental results of Fang et al.¹⁴ revealed that thermal conductivity (TC) and the hardness of asprepared PS exhibited a strong dependence on the preparation conditions, decreasing with increasing porosity. After oxidization at different temperatures, the TC of oxidized PS decreases with increasing oxidation temperatures, whereas the hardness increases significantly. In this work we present a method to improve the stability of PS structures by electrochemical deposition of a silicon capping layer. The influence of the capping layer on the PS hardness and PL stability are investigated.

Experimental

PS was formed by pulse current electrochemical etching of a (100)-oriented n-type single-crystalline silicon wafer with a resistivity of $\sim 1 \Omega$ cm in an electrolyte etching cell. As an electrolyte a mixture of HF(49%):ethanol(95%), 1:4 by volume was used. The mean peak current density was 50 mA/cm², the pulse cycle was

140 ms, and the pause time ($T_{\rm off}$) was 40 ms for an effective time of 30 min. The etching process was explained in detail in our previous work.¹⁵ This was followed by silicon pulsed current electrochemical deposition to provide a uniform silicon capping layer on the porous structure. The method is straightforward because since it does not require any additional chemicals for the electrochemical deposition process. Instead, we use the same etching electrolyte, but this time in a cathodic regime; simply by reversing the current, therefore, the sample will be a cathode and the platinum wire acts as an anode. The cathodic time duration was 10, 15, and 20 min for samples (a), (b), and (c), respectively.

The microhardness measurements¹⁶ were performed with a Shimadzu Micro Hardness Tester HMV-2000 at ambient laboratory conditions. Top and cross-sectional views of the samples were obtained using a scanning electron microscope (SEM). Raman and PL spectra were measured using a 514.5 nm line of an Ar+ laser and He–Cd laser at wavelength of 325 nm as an excitation source, respectively.

Results and Discussion

Electrochemical deposition of silicon capping.— The electrolyte, according to the silicon anodizing reaction, is rich in H_2SiF_6 .¹⁷ In the cathodic regime the reaction could be written as follows

 $a_1 + a_2 = -2$

$$\begin{aligned} H_2 SiF_6 &\rightarrow 2h^4 + SiF_6^- \\ SiF_6^{-2} &\rightarrow SiF_4 + 2F^- \\ SiF_4 &\rightarrow Si^{+4} + 4F^- \\ Si^{+4} + 4e &\rightarrow Si \end{aligned}$$

Accordingly, a thin film of silicon was deposited on the porous layer surface. The deposition rate depends strongly on the current density, while the thickness depends on the deposition time. Different thickness silicon capping was obtained by increasing the deposition time. Figure 1 shows top-view and cross sectional images of samples (a), (b), and (c); the deposition time was 10, 15, and 20 min and the thickness obtained was 1.6, 4, and 7.2 μ m, respectively.

Vickers hardness measurements.— The Vickers test uses a square-based pyramidal indenter with an apex of $\Phi = 136^{\circ}$ causing a diamond-shaped indent on the surface. The Vickers hardness number (HV) is determined based on the test load used when penetrating a Vickers indenter on the sample surface and the indentation area calculated from the indented diagonal length. This leads to the following expression for hardness¹⁸

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Figure 1. Surface SEM images of capped porous samples (a), (b), and (c) and their respective cross-sectional images a', b', and c' showing the silicon cap thickness upon the PS layer.

$$HV = \frac{0.464F}{d^2}$$
[1]

where d(mm) is the mean diagonal length of the diamond-shaped indent and the load (*F*) is expressed in Newton (1 kgf = 9.8 N). The influence of the load on the HV value does not appear in this relation. Because the geometry of the indentation is independent of its size, the hardness is, in principle, independent of the applied load. In practice, however, there is load dependence, particularly for small loads.¹⁹ This is generally attributed to the fact that dislocations and grain boundaries occur only at limited local densities in very small deformed volumes,²⁰ and that the tip of any real indenter may not be perfectly formed to comply with geometric assumptions at very small scales.²¹

Figure 2 shows top-view SEM images of an indentation on a capped PS sample surface using different loads from 0.245 to 1.96 N range. The distorted shape of the square is caused by a slight inclination of the measured surface. The 0.245 N load produces large variation of the indented diagonal length when measurements were repeated. The 0.49 N load, however, produces a more consistent value of diagonal length. Meanwhile 0.98 and 1.96 N loads produced cracks on the samples, hence producing large errors. Therefore the 0.49 N load has been chosen as the load for all hardness measurements.

Individual hardness values were calculated for the three samples [samples (a), (b), and (c)], and a set of three indentations was measured for each sample using the same load. Both diagonals were measured to take into account the eventual asymmetry of the indentation. The indentation depth (*D*) for the Vickers test $\sim d/7$.^{22,23} To avoid the influence of the underlying c-Si substrate, it is required that $D \leq t/10$ (*t*: film thickness).²² For an applied load of 0.49 N



Figure 2. Indentation on a PS capped samples (a), (b), and (c) using loads of 0.245, 0.49, 0.98, and 1.96 N.

and a film thickness of 20 μ m, the above criteria were satisfied for all samples; note that our samples have a porous-layer thickness more than 50 μ m. However, for films or coatings (such as in this work), the measured apparent hardness is the result of contributions by both substrate (the porous layer) and film or coating. Several models exist,²⁴⁻²⁶ however to account for this composite behavior. However, within this study, it is far from our mission to calculate the hardness of the coated film independently; therefore, the hardness results from our samples contributed by both the porous layer and the coated film. The variation of hardness with coated layer thickness is shown in Fig. 3. For comparison, hardness of c-Si(100) has been added in Fig. 3 by a short, horizontal thick line at 11.5 GPa. This value is consistent with Ref. 27 for an applied load of 0.49 N.

The calculated HV shows that an increase in hardness is noticeable with increasing coated layer thickness, and the hardness of all the coated samples is improved compared to the as-anodized PS film. The hardness of as-anodized PS for an applied load of 0.49 N was obtained as 1.2 GPa. This value is somewhat larger than the value of 1.16 GPa by Fang et al.¹⁴ This could be due to some differences in porosity between our samples and their samples. Sample (a) does not show much change in its hardness value compared to as-anodized PS. This could be due to a thin capping layer. Samples (b) and (c) exhibit higher hardness values of 1.82 and 2.9 GPa for an applied load 0.49 N, respectively. For the same porosity, sample (c) has a hardness value two times higher than that of the as-anodized PS sample.

Raman spectra.— In crystalline solids, Raman spectroscopy measures the inelastic scattering of light which results from the



Figure 3. HV as a function of silicon cap thickness for as-anodized PS with applied load of 0.49 N. Typical value for c-Si is also shown as a horizontal bar, indicating the hardness level.

changes in the polarizability of atoms, instead of molecule vibration. Therefore, any effect which may change the lattice spacing and polarizability of crystalline solids, such as stress, temperature, and crystal structure, will result in the changes in the Raman spectra. The Raman peak in c-Si is peaked at 521.0 cm⁻¹; it is symmetric and has a full width at half maximum (fwhm) of 3 cm⁻¹.^{28,29} Amorphous silicon gives rise to broad features at 140 and 480 cm⁻¹.³⁰ Polysilicon, or microcrystalline, gives rise to a broader band around 518 cm⁻¹.³¹

Figure 4 gives the Raman spectra of PS samples (a), (b), and (c) with silicon cap of thicknesses 1.6, 4, and 7.4 μ m, respectively. Also plotted is the spectrum from c-Si (solid thick curve), with peak intensity at 521 cm⁻¹ and fwhm of 3.0 cm⁻¹ (symmetric) and of the PS (without capping) sample (solid thin curve), peak intensity at 516 cm⁻¹ and fwhm of 5.3 cm⁻¹ (asymmetric) for comparison. The Raman intensity from PS (without capping) is 10 times stronger than that from c-Si. Intensity enhancement and redshift (5 cm⁻¹) of the Raman peak of PS (without capping) compared to that of c-Si is believed due to optical phonon confinement in the PS sample.^{32,33} Meanwhile Yang et al.³² have shown that the lattice constant in PS



Figure 4. Raman spectra of capped PS samples (a), (b), and (c). Also shown are the spectra of an as-anodized uncapped PS sample and crystalline silicon for comparison.



Figure 5. PL spectra of an as-anodized PS layer (a) and capped PS samples (b) and (c). The spectra were taken of an as-prepared sample, after 2 weeks and after 2 months.

increases with increasing porosity. This will inevitably create stress (tensile) at the PS/Si interface. Manotas et al.³⁴ have used micro-PL and micro-Raman spectra to determine the stress in the PS. The Raman spectroscopy works have shown that the peak frequency shifts toward a lower wavenumber resulting from stress (tensile) in the Si layer.^{35,36} This suggests that one would expect further redshift of the Raman peak for a layer containing PS. As for sample (a), the peak intensity position is at 517 cm^{-1} and fwhm about 5.3 cm^{-1} . This could be due to a thin Si capping layer (1.6 μ m) on the PS which would cause a little strain relaxation at the PS/c-Si interface, hence causing blueshift (1 cm⁻¹) to the Raman spectra. This argument is supported by the fact that for sample (b) with $4 \mu m$ Si capping, the peak intensity position is at 518 cm^{-1} and fwhm about 6 cm^{-1} . The 2 cm⁻¹ blueshift in sample (b) compared to that of PS without capping suggests that the thicker Si capping is causing further strain relaxation at the PS/c-Si interface and hence, the blueshift in the Raman spectra. As the Si capping gets thicker $(7.4 \ \mu m)$ in sample (c), the peak intensity position of Raman spectrum remains at 518 cm⁻¹, accompanied by a reduction in peak intensity 3 times that of PS (without capping). There could be two possible reasons for this behavior. First, the Raman signal is contributed by the thick Si capping (7.4 μ m), which is suspected to be more polycrystalline or microcrystalline in nature, with peak intensity falling exactly at 518 cm⁻¹.³¹ Second, the Raman signal is contributed by the PS which has reached its optimum strain relaxation, showing no further blueshift. The weaker Raman signal could be due to the fact that the thick Si capping layer was reducing the laser source signal to the porous structure, similarly blocking the Raman signal from the porous structure to the detector. We did not observe a broad peak at 480 cm^{-1} ,³⁰ indicating that there is no substantial contribution to the Raman intensity from possible amorphous Si in the deposited capping layer.

Photoluminescence spectra.— The PL spectra of capped samples (b), (c) and uncapped PS, as prepared, aged in ambient air for 2 weeks and for 2 months, are presented in Fig. 5. The PL spectrum of capped sample (a) is omitted because it is similar to the uncapped PS sample. This is expected because the capping on sample (a) is very thin and should have little significance on the spectrum. Freshly prepared samples showed two main bands. Samples PS and (b) have bands centered at 650 and 670–680 nm which originate from the surface states related to Si–O bonds³⁷ and Si–H bonds,³⁸ respectively. In general, the spectra of all samples are broad. The most widely accepted explanation for this very large width is that

the spectrum is "inhomogeneous," i.e., corresponds to bandgap or near-bandgap emission coming from nanocrystallites with a distribution of sizes.³⁹ For an uncapped PS sample after 2 weeks of aging, the intensity decreases by 20%. After 2 months of aging the wavelength centered at 670–680 nm disappears due to the conversion of Si–H bonds into O–Si–O bonds.⁴⁰ However, the PL band centered at 650 nm increases due to the enhancement of Si-O bonds after aging. The slight wavelength blueshift is attributed to the oxidation of the PS structure, which decreases Si crystalline size and results in bandgap widening caused by the quantum confinement effect.⁴¹ Note that the intensity of the PL changes nonmonotonically, indicative of first a loss of passivation (hydrogen) followed by an improvement in the passivation (oxygen), as the quality of the native oxide improves.⁴² As for sample (b), no aging effects are noticeable, meaning there is no change in PL spectral intensity and no transformation from Si-H to Si-O over a period of 2 months due to the absence of oxidation. In addition, no shift of PL peaks is observable. This indicates that the silicon capping layer (4 μ m) can effectively protect the PS surface from the degradation of PL intensity. For sample (c), the spectra after 2 weeks and after 2 months are similar, with two-band features noticeable at 693 and 719 nm. This is a rather interesting observation, to see a redshift of about 40 nm for both peaks associated with Si-H and Si-O bonds compared to those of PS (as-prepared, without capping). One possible explanation for the redshift is due to the strain (compressive) at the Si capping/PS interface. The strain could be at its maximum value because the Si capping is very thick $(7.4 \ \mu m)$. It is a known fact that the strain causes the bandgap responsible for the spontaneous emission to reduce. This argument assumes that the contribution from the PS/c-Si interface is minimal because the capping is very thick, and the fact that PL laser wavelength is about 60% (325 nm) that of Raman's.

Conclusions

The hardness of PS films on Si substrate and its variation with capping thickness are reported for the first time. The improvement in the hardness and other mechanical properties required for the fabrication of practical silicon-based light emitters was achieved by electrochemical deposition of a Si capping layer. The HV was 1.82 GPa in PS capped with 4 μm Si layer thickness and 2.9 GPa in PS capped with 7.2 µm Si layer thickness, compared to 1.2 GPa in PS without capping, for an applied load of 0.49 N. Our results indicate that the hardness of capped PS samples is enhanced without significantly affecting the optical properties of PS. We have also observed strain variation at the Si capping/PS and PS/c-Si interfaces with varying Si capping thickness. Our results have shown the possibility of fabricating porous materials with optimum mechanical, thermal, electrical, and optical properties.

Universiti Sains Malaysia assisted in meeting the publication costs of this article.

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