

Porous Silicon Formation by Metal-Assisted Chemical Etching

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The method of metal-assisted chemical etching produces a porous silicon layer. Palladium particles are deposited on both: multi-crystalline and Czochralski grown mono-crystalline Si wafers by immersing them in PdCl₂ solution for 1 to 3 min. X-ray photoelectron spectroscopy analysis of Pd clusters shows a decrease in Pd metal fraction by prolonged immersion time t from $F_{Pd} = 71.2\%$ for $t = 1$ min to $F_{Pd} = 61.4\%$ for $t = 3$ min due to Pd oxidation process. Porous silicon forms by metal-assisted chemical etching in a HF:H₂O₂ solution for 1 to 3 min. Photoluminescence of metal-assisted chemical etched samples exhibits the peak with a maximum of t at $\lambda = 650$ nm independent of the etching time. Simultaneously, the intensity of the photoluminescence spectra strongly decreases for extended etching time $t = 3$ min. This behavior is attributed to increasing layer macroporosity, which strongly reduces amount of light emitting nanocrystallites.

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1. Introduction

Since Canham [1] discovered in 1990 visible light emission of porous silicon (PS) under UV illumination, PS attracts a lot of attention as a material for optoelectronic application. The light emission is commonly explained by the quantum confinement model. In this model, the absorption in dimensionally confined silicon wires is responsible for visible photoluminescence. PS is usually formed by electrochemical etching with illumination (n -type Si) or without (p -type Si). It can be also produced by chemical etching in HNO₃:HF:H₂O solution (stain etching). Unfortunately, these two methods are not convenient for mass production, as the first one requires an external bias and the second is slow and unreliable.

Since metal-assisted etching (MAE) requires no external bias and enables fast formation of homogeneous PS layers, it is very promising method of porous silicon formation. The MAE bases on deposition of metal particles (Au, Ag, Pt, Pd) as a catalyst for chemical etching in a solution containing HF and oxidizing species. The thin film of catalytic metal is usually deposited by evaporation or sputtering in vacuum [2–4] or by electroless plating [5, 6].

In this paper we deposit Pd metal particles as a catalyst by immersing Si wafer in PdCl₂ solution for a short period of time (1 to 3 min). The optimization of Pd deposition is carried out by X-ray photoelectron spectroscopy (XPS) and scanning electron microscope (SEM). In the

next step, a metal assisted HF:H₂O₂:H₂O etching forms a porous Si. The photoluminescence (PL) measurement investigates the etching time dependence of the microstructure of porous silicon obtained for durations of MAE in $1 < t < 3$ min range.

2. Experimental and results

The starting material are as-cut multi-crystalline silicon (mc-Si) and mono-crystalline Czochralski-grown CZ-Si (111) wafers with a resistivity $0.5 < \rho < 2 \Omega \text{ cm}$. The samples are immersed in an aqueous solution with PdCl₂ and HCl for electroless deposition of palladium particles on the mc-Si surface.

Figures 1a–c show SEM images of a CZ-Si (111) surface with palladium clusters deposited during immersion in PdCl₂ solution for 1 to 3 min. The dimension of Pd particles varies in the range of $10 < d < 80$ nm. The Pd clusters randomly distribute over the silicon surface and form a density (N_{Pd}) of surface clusters $N_{Pd} \approx 4 \times 10^8 \text{ cm}^{-2}$ after one minute immersion in PdCl₂:HCl solution.

The X-ray photoelectron spectroscopy technique characterizes the wafer after immersion in PdCl₂ solution. The Mg K_{α} X-ray (1253.6 eV, 10 kV, 20 mA) generates core excitations and a hemispherical analyzer (R4000, Gammadata Scienta) acquires the resulting spectra.

Figure 2 displays the Pd $3d_{5/2}$ core excitation spectra for silicon wafer treated in PdCl₂ aqueous solution for different immersion times. The Pd $3d_{5/2}$ spectrum deconvolutes into 2 components: metallic palladium with binding energy $E_{Pd} = 335.3$ eV and PdO with binding energy $E_{PdO} = 336.4 \div 336.8$ eV [7].

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TABLE

The electron binding energies E and ratios F of the Pd $3d_{5/2}$ XPS core excitation components for silicon wafer treated in PdCl₂ aqueous solution.

Pd deposition time t [min]	Metallic Pd		PdO		Pd/Si atomic surface ratio $F_{Pd/Si} \times 10^{-3}$
	E_{Pd} [eV]	F_{Pd} [%]	E_{PdO} [eV]	F_{PdO} [%]	
1	335.3	71.2	336.8	28.8	4.8
2	335.3	69.5	336.6	30.5	6.8
3	335.2	61.4	336.4	38.6	8.9

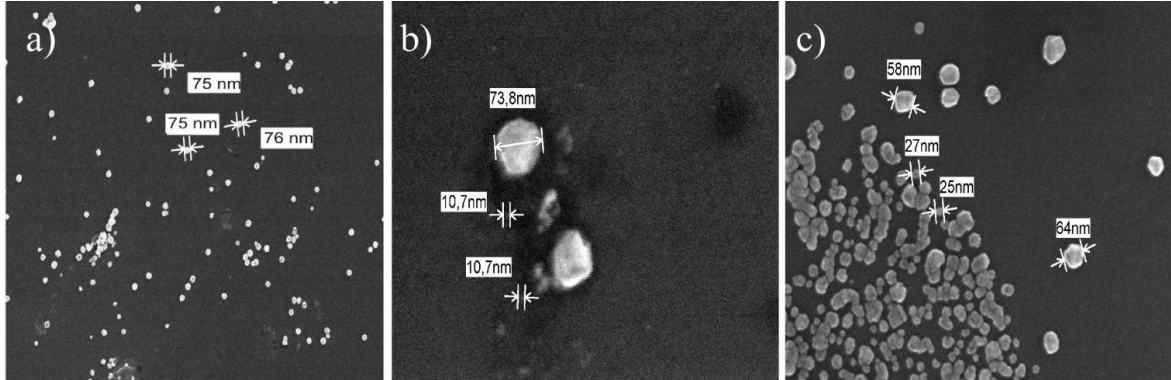


Fig. 1. SEM image of Pd particles deposited on CZ-Si (111) wafer by immersing in PdCl₂:HCl solution for (a) $t = 1$ min, (b) $t = 2$ min, (c) $t = 3$ min. The Pd particle dimension varies in the range of $10 < d < 80$ nm.

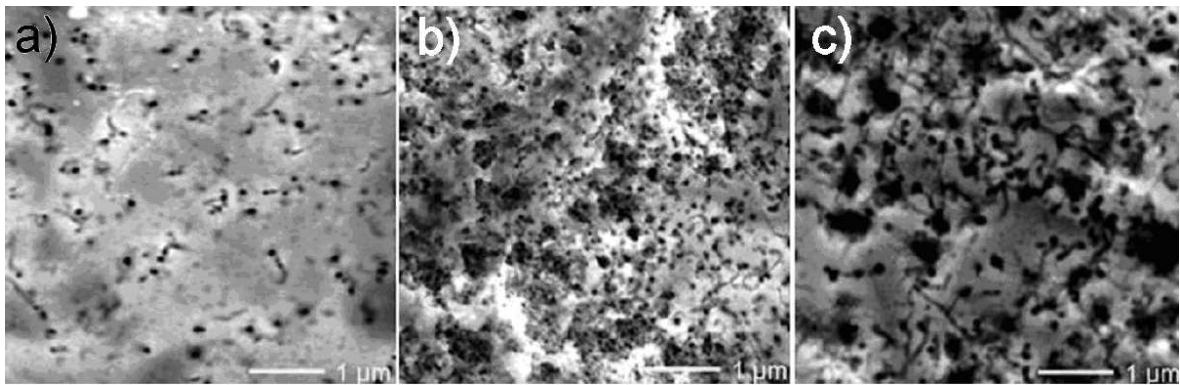


Fig. 3. SEM images of silicon surfaces after MAE during (a) $t = 1$ min, (b) $t = 1.5$ min and (c) $t = 3$ min. The prolonged etching time induces an increase in both macropore density and macropore diameter.

Table and Fig. 2 illustrate that the metallic fraction of Pd clusters F_{Pd} decreases by prolonged immersion time from $F_{Pd} = 71.2\%$ for $t = 1$ min to $F_{Pd} = 61.4\%$ for $t = 3$ min. Simultaneously, the PdO share increases from $F_{PdO} = 28.8\%$ to $F_{PdO} = 38.6\%$ for $t = 1$ and $t = 3$ min respectively. The Pd/Si atomic surface ratio obtained from XPS measurements increases from $F_{Pd/PdO} = 4.8 \times 10^{-3}$ for deposition time $t = 1$ min to $F_{Pd/PdO} = 8.9 \times 10^{-3}$ for $t = 3$ min. These numbers correspond well to the SEM images in Fig. 1a–c, which present larger particles for the systems with prolonged Pd deposition time. The increase of the PdO film coating of the Pd particle core for longer deposition time is related to both: stronger oxidation in the PdCl₂:HCl:H₂O solution and larger Pd particles for the systems with extended immersion time. Due to the catalytic function of

metallic Pd in porous silicon formation it is important to keep the metallic palladium fraction in Pd clusters as high as possible, which favors shorter Pd deposition times. Simultaneously, the Pd deposition time is a compromise between homogeneous porous silicon formation for high Pd particle density by longer deposition time and lower PdCl₂:HCl:H₂O solution usage for shorter deposition time. In the following experiment all samples receive immersion in the PdCl₂:HCl:H₂O solution for $t = 1$ min.

The catalytic effect of the Pd cluster enables etching of the mc-Si wafer in an HF(40%):H₂O₂(30%):H₂O solution in a 25:100:20 ratio. Figures 3a–c display porous silicon formed by MAE in a HF:H₂O₂:H₂O solution for etching times from $t = 1$ min to $t = 3$ min. The prolonged HF:H₂O₂:H₂O etching time induces an increase in both macropore density and macropore diameter.

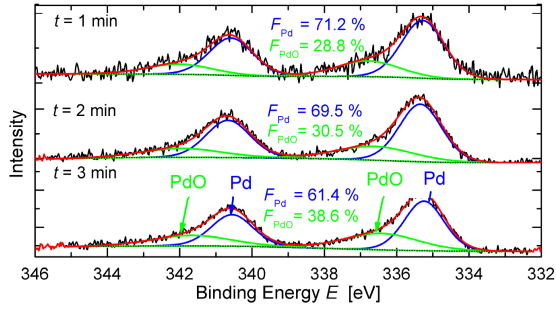


Fig. 2. XPS of Pd cluster for $\text{PdCl}_2\text{:HCl}$ immersion time from $t = 1$ min to $t = 3$ min. With prolonged immersion time the Pd metal fraction decreases whereas PdO fraction in Pd clusters increases.

For detailed porous silicon characterization the setup consisting of a HeCd laser with $\lambda = 325$ nm, a monochromator (Jobin Yvon HR 460) and CCD camera (Jobin Yvon Symphony BIUV) measures the sample photoluminescence spectra under constant laser fluence.

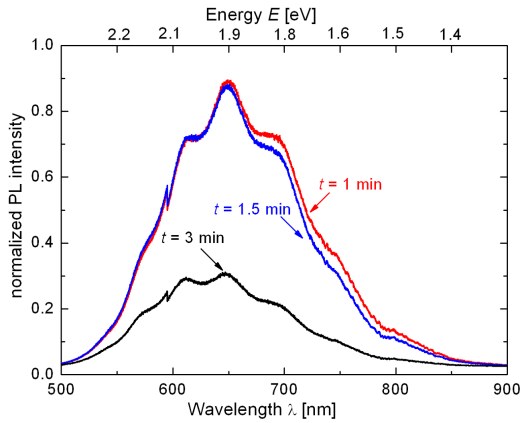


Fig. 4. PL spectra of porous silicon formed on the mc-Si by MAE. The maximum of the PL peak is centered at $\lambda = 650$ nm ($E = 1.9$ eV) with a FWHM = 0.3 eV independent of the etching time. The intensity of the PL spectra strongly decreases for extended etching time ($t = 3$ min) due to increase of layer macroporosity, which reduces amount of the light emitting nanocrystallinities.

Figure 4 displays normalized photoluminescence spectra of MAE porous silicon for different etching times. As illustrated, samples show the strong photoluminescence when exposed to ultraviolet light. Independent from the etching time, the maximum of the PL peak is centered in the red part of the spectrum at $\lambda = 650$ nm ($E = 1.9$ eV) with a full width at half maximum FWHM = 0.3 eV. These results are well understood on the basis of the quantum-confinement model, where the emission energy

$$E = E_0 + \frac{3.73}{d^{1.39}} \quad (1)$$

is shifted towards blue light with respect to the band gap of bulk silicon $E_0 = 1.17$ eV and correlates with the

nanocrystallite size d [8]. Independently of the etching time the nanocrystals with dimension of $d = 3.2$ nm dominate, which is similar to those found for MAE of highly resistive silicon [9]. Simultaneously, the intensity of the PL spectra strongly decreases for extended etching time $t = 3$ min. This behavior is attributed to the increase of layer macroporosity, which strongly reduces amount of the light emitting nanocrystallites. Figure 3c validates this assumption as it shows a higher macroporosity of the sample and bigger macropore diameter after three minute etching.

3. Conclusion

This paper shows that immersion of Si wafer in PdCl_2 solution creates nanometer sized palladium clusters as a catalyst for MAE. It is found that the optimal time of Pd deposition is one minute. Longer immersion time causes Pd oxidation and increases size distribution of the Pd clusters. Short time of Pd deposition is profitable for industrial application due to lower PdCl_2 solution usage and still homogeneous formation of light emitting porous silicon.

The maximum of the PL peak is centered in the red part of the spectrum at $\lambda = 650$ nm ($E = 1.9$ eV) and it is independent of $\text{HF:H}_2\text{O}_2\text{:H}_2\text{O}$ etching time. On the basis of the quantum-confinement model the nanocrystals with dimension on $d = 3.2$ nm dominate in porous silicon formed by MAE. Simultaneously, the intensity of the PL spectra strongly decreases for extended etching time $t = 3$ min. This effect can be explained by lower density of nanopores and higher density of macropores for longer etching times.

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