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Study of anodization parameters effects on photoconductivity of porous silicon

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Abstract We have prepared porous silicon by etching p-type crystalline silicon in different conditions such as: varying electrolyte concentration, current density, and etching time. The primary objective of this research is to develop a scientifically based technique for the measurement of photosensitivity. One such technique involves measuring the photoconductivity of the porous silicon under halogen lamp irradiation. Our photoconductivity measurements agree with photoluminescence measurements in previous work, and demonstrate the direct transition of porous silicon. Varied etching conditions change the peak of photoconductivity from 600 to 520 nm (from 2.13 eV to 2.4 eV) as the porosity of the layer gradually increases, and the photoconductivity band also becomes slightly more intense. The photoconductivity peak shift toward shorter wavelength was interpreted to be the result of band gap widening. We observe two distinct regimes in the time decay of photoconductivity, fast decay and steady state, that arise from the recombination process and electron–hole asymmetry near the Fermi surface. Experimental measurements of photoconductivity give useful information about the band gap, band structure, and variation of transport properties due to the micro-structural porosity created during the etching process.

Introduction

Porous silicon (PS) has attracted much attention for its photoconductivity (PC) and photo luminescent properties for potential use in optoelectronic and microelectronic applications. Scientifically, photoconductivity represents an important tool for the study of transport of photo-generated charge carriers. PC effects are important from both the viewpoint of photovoltaic applications and the interaction of external electric fields with photoluminescence (PL) emission. The principal aim of studies carried out on PS has been to fabricate a stable and efficient light-emitting diode (LED) compatible with existing silicon technology. General theoretical and experimental works on these subjects can be seen in Refs. 1–5. Emission properties of PS have been studied in detail [2–4], especially with the use of PL, photoluminescence excitation (PLE), and also with other emission techniques like electroluminescence (EL) [4, 6]. On the other hand, PS layers have commonly been detached from the substrate for optical absorption studies of the band-gap.

The photoconductivity of PS has been reviewed by many authors. Frello et al. [5] have undertaken a systematic study of PS by combining PL and PLE with PC, which is based on photoabsorption and may yield information about absorption properties of PS. Gorbach et al. [7] have used PC investigation of PS for solar irradiance detection. Dafinei et al. [8] showed that PC measurements demonstrated the existence of a

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junction electric field able to separate electron–hole pairs. Sedlacik et al. [9] presented that it is possible to spectrally separate the Si substrate PC from the response of the PS layer.

Photoconductivity is a complex phenomenon involving competition between charge carrier generation, recombination, trapping, and transport. Measurements of PC have been used to study electronic transport properties in semiconductors and insulators [10]. Since the generation of electrons and holes is the first step in any photosensitivity process, measurement of PC provides fundamental information on the density, mobility, and the lifetimes of these carriers generated in PS.

The PC spectral response is a measure of band-gap widening in PS. In addition, carrier lifetime is determined from analysis of the dynamic response of PC and is a key parameter for discussing carrier transport mechanisms in PS, and possibly for EL characteristics [5]. The nature of the band-gap in PS is still an issue of debate. While it is known that the band-gap of bulk crystalline silicon is increased by quantum confinement effects in small particles, a reliable theoretical expression for the optical absorption of PS is not yet available [11].

In this paper, considering quantum confinement concepts in nanometer-scale particles, we have investigated the effect of production conditions on the pores of PS on Si wafers, and present new PC data from p-type PS.

Experimental details

Our PS samples were prepared by the standard electrochemical anodization method with preparation details as reported in our previous work [12, 13], where results of some of our measurements are also reported. The physical characteristics of the Si wafers used are p-type with 0.28 mm thickness, float zone, (100) orientation, and 1.4–2.6-Ω·cm resistivity. The Al-ohmic back contact was coated with a vacuum evaporation system (HIND HIVAC Model 12A4-DM) and annealed at 400 °C for 30 min. The contact was attached to a copper wire with silver conductive paste and totally sealed with black wax. Anodization was carried out in a Teflon beaker with hydrofluoric acid (HF) (40%); ethanol (98%); distilled water with various current densities for several etching times, always at room temperature. We denote the relative proportions of the three components solution by (x:y:z), respectively. After etching, the wafers were removed and dried without rinsing. The existence of a porous layer on the samples was easily verified by optical microscopy. While not directly observed in this study, typical porous layers exhibit a filamentary structure with radius ~6 nm and layer thickness ~2 μm [12]. A 20 nm layer of gold film with maximum transmittance of 32% was evaporated over the PS surface to create a semitransparent electrical contact without filling the pores; effectively maintaining the high surface area of the device. A schematic diagram of the device is shown in Fig. 1.

PC measurements were preformed on the gold PS junction device shown in Fig. 1. The specimen holder was enclosed in a metal box to shield the specimen from room light and electrical noise. One silver wire was connected to a gold pad (as a semitransparent thin layer) of the sample, and the other connected to the pin in electrical contact with the backside of the sample. The silver wires on the specimen were connected to a Keithley 610C electrometer. The 610C electrometer has a built-in DC voltage source that is used to apply an external bias voltage to the specimen (typically 10 V).

A 100 W halogen lamp was coupled to one of a set of optical filters, and used for illumination. The optical filters used have 40 nm wide (FWHM) passbands with center wavelengths in the range of 400–700 nm. All data reported here were measured at room temperature.

It has been shown that contact gold–PS is nonlinear and its properties may influence observed characteristics. To distinguish the contribution of gold–PS contact and the behavior of PS, we repeated current measurements in illumination by applying bias voltage to the surface of PS with gold. Our results clearly show that the contribution of gold–PS contact is very weak, less than 10^{-3}, and cannot play a major role in the behavior of PS. In the other words, the current

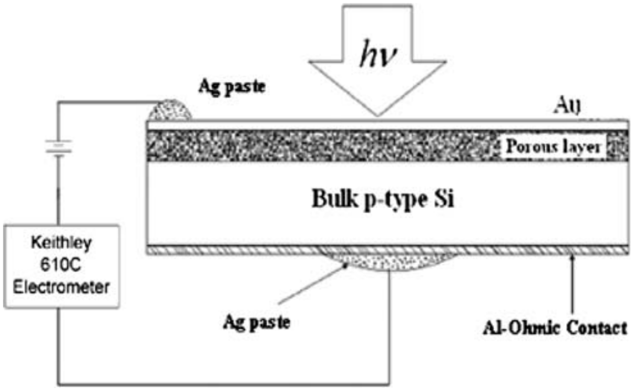

Fig. 1 Schematic of the gold PS junction device

through structure are really determined only by conductivity of PS.

The PC current data of our PS samples depends on the wavelength of light. So, we normalized the PC current data for all measurements to get better comparison between the results.

Results and discussion

Typical PS samples were prepared in a (1:1:1) electrolyte, etching for 30 min at a current density of 2 mA/cm^2. A characteristic property of our typical PS samples is that the pore structure varies little with changes in electrolyte composition, etching time, or current density. In Fig. 2 the PC signal for a typical PS sample has been plotted versus the wavelength of the illuminating light. This curve shows that the PC peak is at 600 ± 20 nm (2.13 ± 0.06 eV). Alternatively, we measured PL intensity versus wavelength for typical samples [13]. PL has been a valuable technique for studying intra- and inter-defect or defect band electronic transitions, in addition to band-to-band and the exciton transitions. The PL measurements showed a peak emission at approximately 600 nm (2.13 eV) with a bandwidth (FWHM) of nearly 80 nm.

To guarantee experimental reproducibility, all PS samples were stored in the dark before each measurement, and the dark current was measured continuously. In all measurements reported here, illumination was not preformed until the dark current was observed to stabilize entirely.

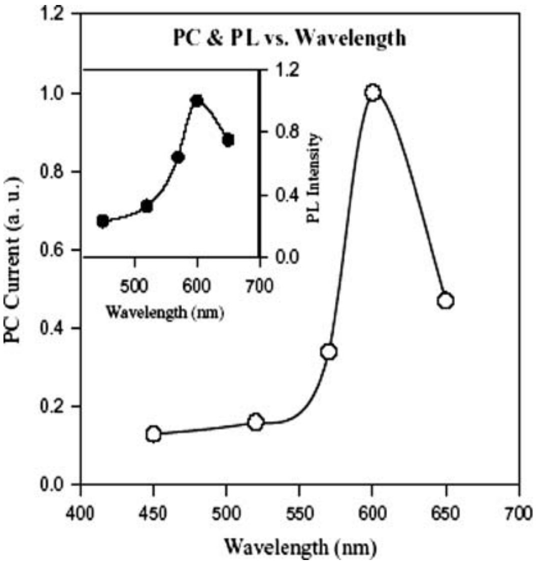

Fig. 2 Photoconductivity (PC) current and photoluminescence (PL) intensity for a typical porous silicon (PS) sample

As a further check on the reliability of the spectral information, the gold film's spectral response was measured. A gold film similar to that on the samples was deposited on a glass slide and its spectral transmission measured and compared with that of the underlying glass, measured separately. In the region from 400 nm to 700 nm, the variation in transmission was the same. Above 750 nm, the gold showed a 20% increase in absorption. However, since the PC spectral response was below 700 nm, it would not be affected.

As shown in Figure 2 the PC peak occurs at the same visible wavelength as the PL peak, demonstrating that the pores in the Si structure change the band gap from the infrared to the visible region. Our measurements are in agreement with data for the optical band gap corresponding to the energy of PL [14]. As discussed in Ref. [12], electroluminescence (EL) is very weak, and most of the researchers do not believe it to be representative of the majority of the PS material [15]. While the PL peak in our films occurred at 600 nm or 2.13 eV, which corresponds with our PC measurements (i.e. the optical band gap), derivation of the precise value of the band gap of a semiconductor from optical absorption is a non-trivial task, requiring an expression for the shape of the absorption or reflectance as a function of light energy. The nature of the band gap in PS is still an issue of debate [11], though perhaps best described as the crystalline Si band gap, broadened by quantum confinement effects in small particles. A reliable theoretical expression for the optical absorption of PS is also not yet available. Therefore, we cannot give a precise value for the band gap in our films, but the measurement results in Fig. 2 show maxima at 2.13 eV.

Figure 2 shows our sample has peak PC at 600 nm and its PC drops at shorter wavelengths, below 600 nm. This is in agreement with general physical expectations, as the PC spectrum from c-Si has a peak at 1100 nm and its PC drops below 1100 nm. In PS the PC peak from 1100 to 600 nm and PC reduction below 600 nm can be explained by crystalline Si photoconductivity or could be due to surface recombination losses of carriers generated in the region very close to the Al contact.

Physical properties of PS layers, such as porosity, thickness, pore diameter, and micro structure, depend on the anodization conditions. These conditions include HF concentration, pH of the solution and its chemical composition, current density, wafer type, resistivity, crystallographic orientation, temperature, anodization etching time, and illumination (or not) during anodization. Optimum control of fabrication

Table 1 List of samples with different etching time, (*Typical PS sample)

	Electrolytes Concentration (x:y:z)	Current Density (mA/cm^2)	Time (min)
1*	1:1:1	2	30
2	1:1:1	2	45
3	1:1:1	2	60

Table 2 The list of samples with different current density, (*Typical PS sample)

	Electrolytes Concentration (x:y:z)	Current Density (mA/cm^2)	Time (min)
1*	1:1:1	2	30
4	1:1:1	10	30
5	1:1:1	30	30

and reproducibility are only possible if all the parameters are carefully controlled [16]. The effect of varying anodization conditions is studied by comparing the resulting PC peak position with various samples:

(i) *Etching Time Effect*: Electrolyte concentration and current density were kept constant, and etching time was increased to double that of the 'typical' sample (Table 1). The reliable etching time was obtained from our previous experiments [12]. We found the PC peak changed from 600 nm to 520 nm with doubled etching time. Figure 3 shows this difference.

(ii) *Current Density Effect*: Maintaining constant electrolyte concentration and etching time the current density was increased from 2 mA/cm^2 for the typical sample to 10 and 30 mA/cm^2 (Table 2). We found PC peaks at 600, 570, and 520 nm for 2, 10, and 30 mA/cm^2, respectively (Fig. 4).

(iii) *Electrolytes Concentration Effect*: In this experiment the electrolyte concentration varies from (1:1:1) to (2:1:1) and (3:1:1), i.e. the amount of HF varied (Table 3). The current density and etching time were kept constant. We found the PC peak shifted from 600 nm to 520 nm (Fig. 5).

These three experiments may help clarify pore formation in the direction of etching, and lateral pore growth in Si. The surface structure of PS is known to be nano-scale [9], creating complicated electrical transport properties as compared to lower porosity material. Quantum confinement results in modulation of the effective band gap creating fluctuations that have a major impact on electrical transport because they increase scattering and cause carrier localization. Therefore, the resistivity of the material is higher than that of low porosity layers by a few orders of magnitude [9].

Some fundamental points regarding the photo-electric response of PS with the change in etching time/electrolyte concentration/current density have been clarified. The observed photoconduction characteristics can be interpreted to be the result of the band-gap widening in PS with increased etching time/current

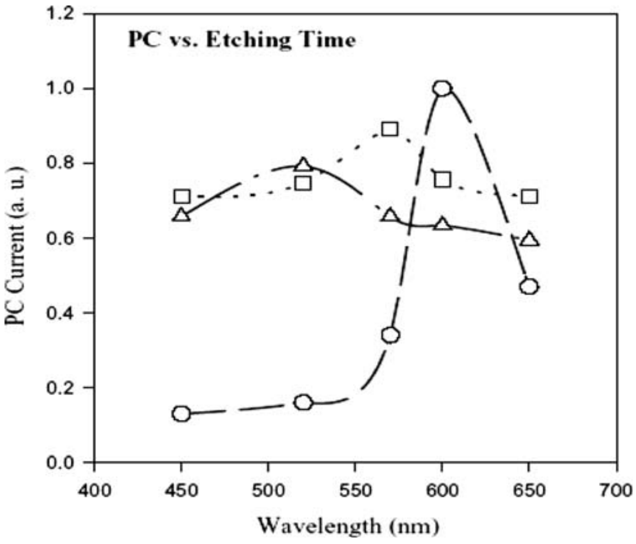

Fig. 3 Etching time effect on PC. With increasing etching time, the PC peak has shifted from 600 nm to 520 nm (Sample No.1 ○, Sample No.2 □, Sample No.3 Δ)

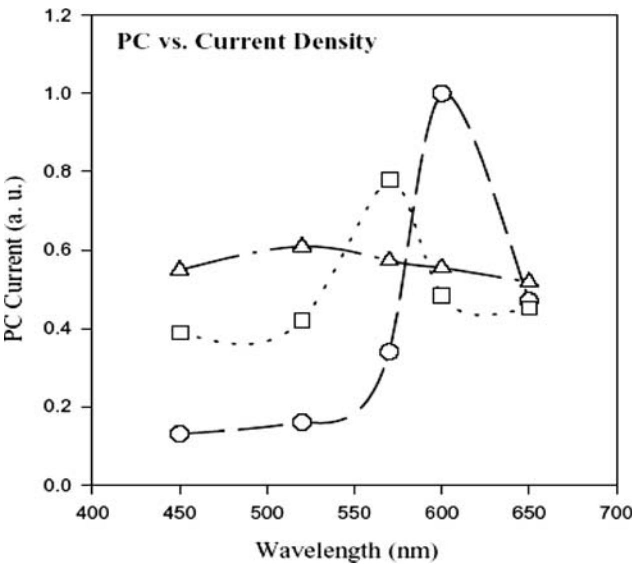

Fig. 4 Current density effect on PC. With increasing the current density, PC peak has changed from 600 nm to 520 nm (Sample No.1 ○, Sample No.4 □, Sample No.5 Δ)

Table 3 The list of samples with different Electrolytes Concentration (*x*:*y*:*z*), (*Typical PS sample)

	Electrolytes Concentration (x:y:z)	Current Density (mA/cm^2)	Time (min)
1*	1:1:1	2	30
6	2:1:1	2	30
7	3:1:1	2	30

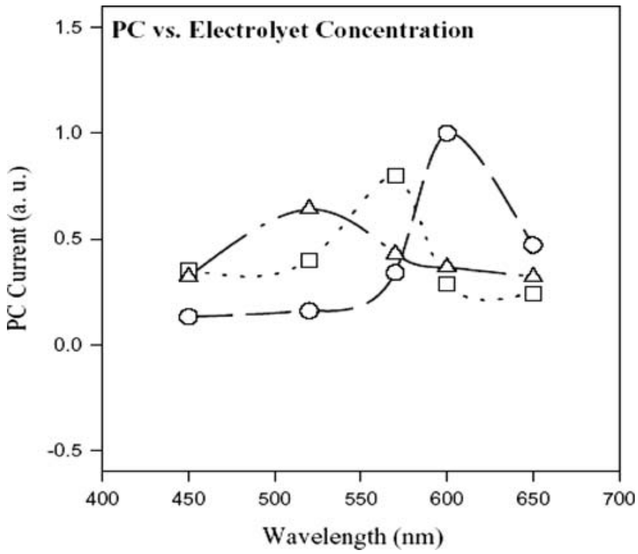

Fig. 5 Electrolyte concentration effect on PC. With increasing electrolyte concentration, PC peak has changed from 600 nm to 520 nm (Sample No.1 ○, Sample No.6 □ , Sample No. 7 Δ)

density and electrolyte concentration. Our results show similar behavior to those of Mehra et al. [17], as we found the same blue shift from 600 nm to 520 nm for all anodization parameters and they claimed various blue shifts for each anodization parameters. A possible explanation for the difference could be using various p-type Si wafers for the preparation of PS, our Si wafers are 1.4–2.6 Ω·cm and theirs are 1 Ω·cm.

The observed results are attributed not to an alloying effect, in an amorphous phase or siloxene as has been previously suggested [4], but to a quantum size effect, for the following reasons. First, the PC peak shifts to lower wavelengths in visible region with its color changing from yellow through green to blue. Second, our results demonstrate that the PC current decreases appreciably during simple chemical dissolution in aqueous HF. Third, the spectral half-width of the PC current increase appreciably but always remains narrower than the 0.3 eV wide band of amorphous Si [18], and much narrower that the bands from polysilane alloys (FWHM 0.6–0.7 eV) that also emit in the visible region [19].

Dependence of PL and PC peak location on quantum size effects is described in references [9, 20]. Electrolyte concentration and etching time in the electrochemical etching process play a similar role as the anodic current density. When anodically biased at low current densities, pores form on the surface of Si substrate and propagate into the bulk in a very well organized manner causing a highly columnar Si skeleton to be left behind. So the nano-structure of PS depends on chosen production process, as described above, as well as on some other specific factors, for example the type and resistivity of the initial substrate [21], anodization temperature [22], and any post fabrication treatments [23].

Porosity of the PS samples was determined by a gravimetric method [23]. PS sample No. 1 had porosity of about 30%, samples No. 2, 4, and 6 had about 50%, and samples No. 3, 5, and 7 had about 70%. We can see that overall porosity of PS depends on anodization parameters, rising with anodization time, current density, and HF concentration. According to the quantum confinement mechanism, increasing PS porosity shrinks the size of silicon nanoparticles toward the atomic scale, then the PS develops cracks and small growing pores begin again. Consequently, the PC peak position shifts to higher energy (lower wavelength) and it can be interpreted by band gap widening in PS.

The behavior of PC versus time is shown in Fig. 6. Illumination of the sample was initiated at time zero and terminated at $t = 90$ min. The reduction of PC in this figure has two distinct parts. At the beginning of

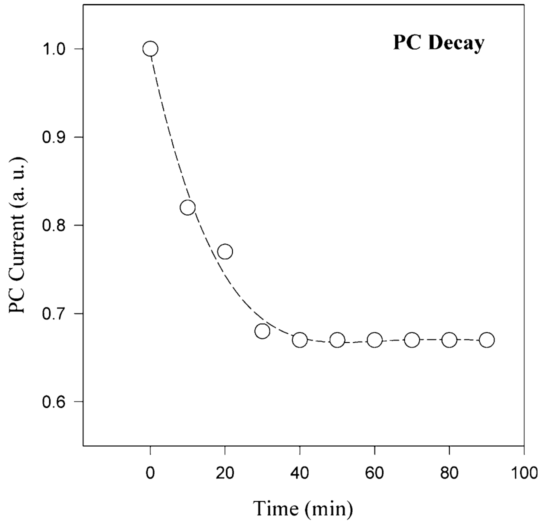

Fig. 6 Photoconductivity time response for a typical sample, obtained while continuously illuminating with light. In the curve, illumination was initiated at time $t = 0$, and terminated at $t = 90$ min

illumination, there is a rapid increase in the current and the height of this step in the signal is normalized at time $t = 0$. The time scale of this increase was less than a few milliseconds. This time is negligible in comparison to the reduction time. The large rise in PC for all specimens following light exposure is indicative of a high concentration of photogenerated electrons and holes, which directly or indirectly participate in a photosensitivity reaction. Fresh PS samples have electronic quantum structures that generate high photoconductivity current. While time elapsed in the PC measurement, the PS samples were exposed to an air environment, and gradually formed a thin surface insulator layer of siloxene ($Si_6O_3H_6$), reducing the PC current to a persistent value within approximately 30 min. For all of the curves, the illumination was not interrupted until the current through the sample had been stabilized.

After the initial rapid increase, the photocurrent decreases slowly and stabilizes finally at a level that is below the initial dark current level. This drop in PC is possibly due to the trapping of the conduction electrons by surface defects in the PS specimen. Our results are in agreement with well-established results [5].

Conclusion

We have presented results in the field of solar cell technologies and photo detectors. In this area, we have demonstrated the use of a simple and controllable method to fabricate porous silicon on mono-crystalline wafers to increase optical efficiency. We obtained reliable anodization conditions and nominated a typical sample (sample No. 1), then characterized the effect of anodization parameters such as etching time, electrolyte concentration, and current density.

In conclusion, we found that increasing etching time, current density, or electrolyte concentration, created smaller silicon pore size and higher porosity, shifting the photoconductivity peak from 600 nm to 520 nm. This shift in the spectral distribution of the PC of the device is indirect evidence of the change in porous silicon microstructure, as opposed to direct observations from others with, for example, scanning electron microscopy [24]. These results are in agreement with PL measurements [12], with the peak of PL shifted to shorter wavelength as the porosity increased. The time response of PS reveals a decrease in current over approximately an hour that is permanent, and believed to be caused by generation-recombination on the surface. Our results agree with the quantum confinement model of PS and suggest that the origin of PC is related to quantum wires in the porous layer.

In general, we can say that for PS, the study of photoconductivity and transport is still in its infancy. At this stage it is necessary to exclude errors and to clarify what information we can obtain from different techniques. In this sense the above PC results obtained on PS represent substantial progress and open the way for the use of PC techniques for optimization of PS transport properties, important for PS-based EL devices.

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