

# Photovoltaic response in electrochemically prepared photoluminescent porous silicon

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Received 27 February 1992

Using the electrochemical procedure for the production of porous Si, material is produced which shows a solid state photovoltaic response. Under simulated sunlight, the open circuit voltage is near 0.36 V and the photocurrent is near 2  $\mu$ A. The current–voltage characteristics exhibit a high series resistance which is on the order of 1 M $\Omega$ . The spectral response is characteristic of the silicon itself, and suggests that a heterojunction is formed between the high effective bandgap porous silicon and the bulk p-silicon wafer. Time resolved photoconductivity measurements indicate that the porous Si material is characterized by a high recombination rate. At low excess carrier density there is a barrier to this recombination which is tentatively ascribed to band bending and carrier injection at the porous Si/crystalline Si interface.

## 1. Introduction

It has recently been demonstrated that electrochemically produced porous Si can exhibit photo and electroluminescence [1,2]. It is the light emitting diode, or LED, structure that most researchers are currently investigating using this material. Electroluminescence implies that the reverse process can also be possible. A solar cell or detector can be made from an optoelectronic material [3,4]. This paper describes the photovoltaic effect observed from a solid state porous silicon–silicon structure. The current–voltage characteristics, spectral response and time resolved photoconductivity are described for porous Si on p-Si.

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2. Experimental methods

The procedure for the formation of the porous Si is described elsewhere [1,2] Boron doped p type (100) Si wafers (Siltec 15  $\Omega$  cm) were anodically etched in 20% HF in ethanol for 10 min at 20 mA/cm<sup>2</sup>. The back contact was a sputtered Au layer which was approximately 500 nm thick. Visible red photoluminescence was observed under UV light after etching, as is described in the literature [1,2]. After drying the treated water in nitrogen at 25°C, a Pt needle probe was used to contact a small area of the porous Si surface. Fig. 1 shows the arrangement used to produce a photovoltaic effect. Under air mass 1.5 (AM1.5) light from an Oriel

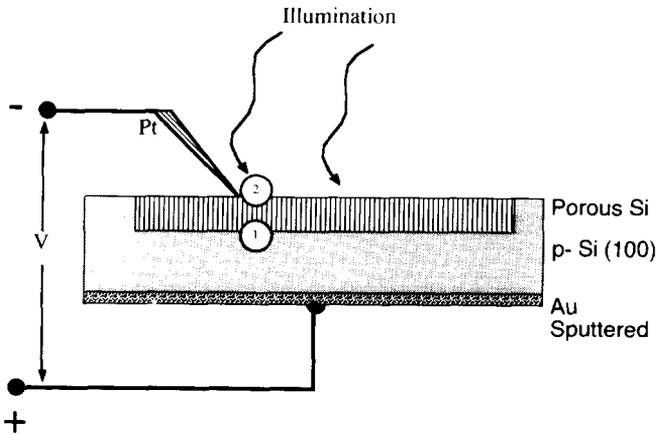


Fig. 1. Configuration used to observe a solid state photovoltaic effect with porous Si. The numbers indicate two possible photovoltaic interfaces present.

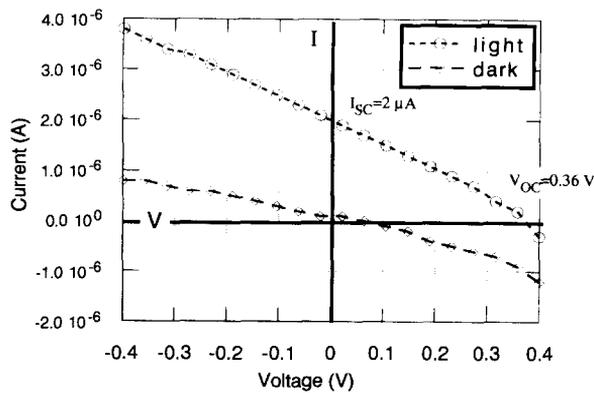


Fig. 2. Current–voltage characteristic for the device in fig. 1 in the dark, below, and under simulated solar illumination (100 mW/cm<sup>2</sup>), above.

81101 solar simulator, the current–voltage characteristic shown in fig. 2 was obtained. The photocurrent spectrum was then resolved using a Kratos monochromator. Time resolved photoconductivity measurements were taken using the procedure in the literature [5].

### 3. Results and discussion

#### 3.1. Current–voltage characteristics

The arrangement in fig. 1 yielded the photoresponses shown in figs. 2 and 3. The results of fig. 2 illustrate that a photovoltaic effect is observed. The results were obtained for porous silicon without an applied contact pad. The dark characteristic in fig. 2 is shifted upward upon illumination in a fashion characteristic of a solar cell or detector with a very high series resistance [3,4]. Indeed, the calculated resistance from fig. 2 is on the order of 1 M $\Omega$ . Open circuit voltages,  $V_{OC}$ , observed were in the range of 0.3–0.4 V. Due to the unknown area that is contacted, the current density and conversion efficiency could not be calculated. If the contacted area is large, 2  $\mu$ A produced in short circuit,  $I_{SC}$ , indicates a low conversion efficiency. It was hoped that a Au contact pad could be applied to interconnect the photoactive regions of the porous layer. Attempts to cover the porous Si layer with a thin (50 Å) layer of Au, Al or Pt did not result in a significant improvement of the photoresponse. If the Pt wire contacted a clean area of the wafer without porous Si, only a few millivolts were observed. This is consistent with the literature, since it is known that Pt forms an ohmic, and not a Schottky, contact to p-Si [3]. We are therefore proposing that the observed effect is due to a heterojunction between the bulk Si and the porous Si layer (interface 1 in fig. 1). Since the porous Si is believed to possess a bandgap larger than Si, the

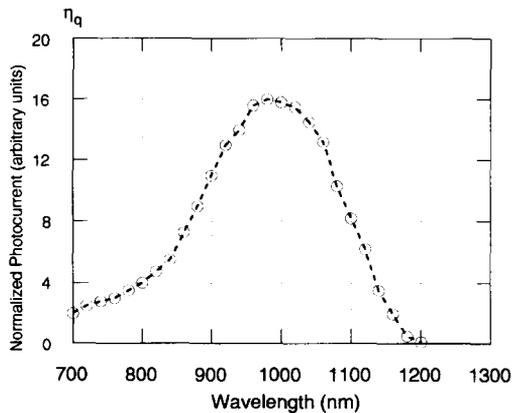


Fig. 3. Normalized photoresponse of the porous Si device. This is expressed as the current collection efficiency as a function of wavelength [3].

arrangement in fig. 1 would be similar to that used for CdS-Si or ITO-Si [3]. The porous Si would then serve as a window layer, with the bulk Si functioning as the main light absorber. As depicted in fig. 1 it is then likely that the photoeffect comes from the Si-porous Si interface, indicated in the diagram as 1, instead of from the porous Si-air interface, indicated as 2. EBIC or spatially resolved studies could confirm that this is the interface responsible for the effect [3]. The low rectification in the dark characteristic could indicate a band diagram for two materials such that both Fermi levels are initially at the same energies. Under illumination, however, the Fermi levels of the porous Si shift and a space charge layer could be formed with concurrent band bending [3]. The observed polarity, i.e. bulk Si as positive, is consistent with this model. Solid state rectification in the dark has been observed for porous Si at higher voltages and currents [6]. This can be attributed to the high series resistance of the porous layer. It has been proposed that illuminated porous Si should yield higher photovoltages than for normal Si solar cells (0.5–0.6 V) [4]. In order to realize this in practice, the porous layer would then need to be deposited on a material with the proper or work function, or Fermi level, so that the maximum band bending could be realized in a Schottky or heterojunction diode [3].

### 3.2. Wavelength response

The photocurrent spectrum shown in fig. 3 was normalized to the known photon flux at each wavelength. It then represents the current collection quantum efficiency,  $\eta_q$ , or photoresponse [3]. The spectral response shown in fig. 3 indicates that the wavelength cut-off is due to the bandgap of bulk Si (1.12 eV). The nature of the sharp decrease at shorter wavelengths is uncertain at present, but is indicative of a Si detector with a high surface recombination velocity [3]. Light of shorter wavelength is absorbed closer to the surface. Carriers that are created near the surface of the porous Si should therefore recombine with a higher probability than in the bulk Si. If interface 2 in fig. 1 was responsible for the photoeffect, a better response in at short wavelengths would be expected.

### 3.3. Charge carrier kinetics

Contactless time resolved microwave photoconductivity, TRMC, measurements were performed in order to study the charge carrier recombination [5]. The same p-Si wafer was measured with three different surfaces: a bare Si surface chemically etched in 0.5 M HF, a Si surface with thermally grown SiO<sub>2</sub>, and a porous Si surface. These studies are then similar to those made for chemically treated non-porous Si [7]. TRMC signals were induced by 532 nm light pulses of 10 ns (FWHM). Assuming that the material has an absorption coefficient of 10<sup>4</sup> cm<sup>-1</sup>, at 532 nm, this leads to an initial excess charge carrier distribution concentrated in a 1–2 μm thick layer at the illuminated surface. Since the decay behavior extends over a large time range, the TRMC signals are displayed on a double logarithmic scale in fig. 4. The experimental results show that no appreciable decay occurs

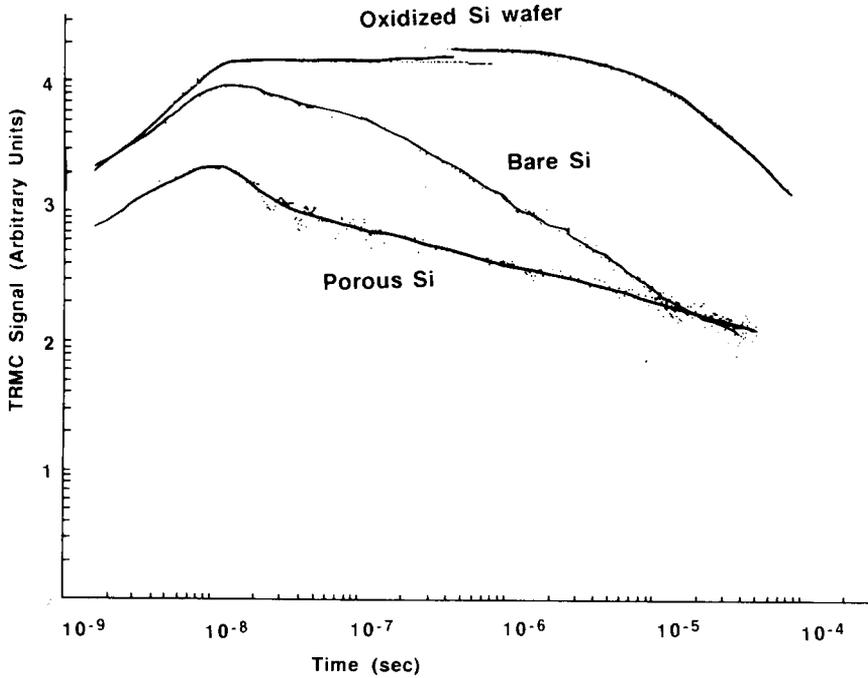


Fig. 4. Double logarithmic representation of the time resolved microwave detected photoconductivity, TRMC [5], for the porous Si structure in fig. 1 (bottom plot), compared to the bare Si (middle) and thermally oxidized Si wafer (top). The excitation wavelength was 532 nm with an excitation density of  $0.5 \mu\text{J}/\text{cm}^2$ .

within the first two micro seconds in the wafer with the surface passivated by an oxide layer. Consequently, the decay observed in the bare Si wafer, and in the wafer with a porous Si coating is due to surface recombination. The signal height immediately after excitation at 10 ns is the highest in the wafer with the protective oxide surface, and the lowest for the wafer with the porous Si layer. This implies that during the excitation, surface recombination takes place at the bare Si surface and the porous Si surface. The surface recombination rate at the porous Si surface is the largest. It seems reasonable to attribute the surface recombination in the wafer with the porous surface to recombination within the porous Si layer. At least part of this surface recombination then gives rise to luminescence observed in this wafer.

After the initial surface recombination, the remaining mobile carriers will partially diffuse in the direction of the non-illuminated face of the wafer. After 10 ns, the decay in the bare Si wafer is clearly faster than in the porous wafer (fig. 4). This decay is also due to surface recombination. This may seem strange since the porous Si surface is characterized by a higher recombination rate than the bare Si, as was concluded from the initial TRMC signal height. The decay after 10 ns must therefore be due to a decrease of the surface recombination rate with the time

since excitation, and with the excess charge carrier density. The most probable reason for this phenomenon is the presence of a space charge region at the heterojunction between the porous and non-porous Si. Initially, at high excess carrier density, the bands are flat. At a later time, band bending in the space charge region is restored and hinders recombination due to injection of carriers into the bulk Si. It must be noted that the decay in the bare Si wafer is explained by diffusion controlled surface recombination via a very large carrier sink at the surface [3,7]. The results of the porous Si signal can be explained by charge carrier injection into the bulk Si due to band bending at the heterojunction indicated as 1 in fig. 1.

The existence of electroluminescence in solid state porous Si devices has been established using applied AC or DC voltages [6]. The mechanism for this effect is not yet clear. It can be due to a high series resistance heterojunction diode, or a high field recombination mechanism similar to that of ZnS particles in large area electroluminescent displays [8]. If the porous Si particles are suspended in a dielectric medium ( $\text{SiO}_2$ ) in this way, then the fabrication of efficient detectors using porous Si will be difficult due to high resistivity and low current extraction efficiency. Further experiments are required to verify this hypothesis.

#### 4. Conclusions

The existence of photoluminescence in Si implies that one could create detectors and solar cells with higher photovoltages than in normal Si [4]. A photovoltaic effect has been demonstrated using porous Si on p-Si. The effect appears to be due to a heterojunction between the porous and non-porous Si, with the concurrent generation of a space charge layer and carrier injection upon illumination. Further studies are needed, however, to establish the nature of the photovoltaic interface. The  $I$ - $V$  characteristic is indicative of a device with a high series resistance. This could limit further development of this material as an efficient detector. At the least, the photovoltaic effect can be used in the future to characterize the layers used in electroluminescent porous Si devices.

#### Acknowledgements

The authors wish to thank Peter Sutter, of the Zurich Laboratory for Festkörperphysik, for determining the spectral response of the material and Dr. Axel Richter, of the Munich Fraunhofer Institute, for valuable discussions on the electroluminescence of n-porous Si.

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