

**OPTICAL, THERMAL AND CARRIER TRANSPORT PROPERTIES  
OF POROUS SILICON LAYER DETERMINED USING  
PHOTOACOUSTIC SPECTROSCOPY**

**By**

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**Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia,  
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of the requirements for the degree of Doctoral of Philosophy

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**Chairman: Professor W. Mahmood Bin Mat Yunus, PhD**

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In this study, porous silicon layers were fabricated on p-type and n-type silicon substrates by electrochemical etching method at five different current densities (i.e. 16.98, 22.64, 28.29, 33.96 and 39.62) mA/cm<sup>2</sup>. The etching duration was fixed at 20 minutes. In the second series of preparation, the silicon substrates were anodized at six different etching durations (i.e. 20, 25, 30, 35, 40 and 45 minutes) with constant current density of 22.64 mA/cm<sup>2</sup>. Photoluminescence spectra, measured by fiber optics spectrophotometer show a peak that is blueshifted towards higher energy as the porosity is increased.

Photoacoustic spectroscopic technique was used to characterize the optical, thermal and carrier transport properties of the samples. The measurements of the optical properties were carried out at three different modulation frequencies (15 Hz, 23 Hz and 33 Hz). The absorption peaks show a gradual blueshift towards higher energy as the porosity is increased. The band gap energies of the porous silicon layers were determined from the

photoacoustic spectra measured at modulation frequencies of 23 Hz and 33 Hz, respectively. The band gap increases linearly with porosity from 1.80 eV to 2.00 eV for the porous silicon prepared on p-type silicon substrate, and from 1.70 eV to 1.86 eV for the porous silicon prepared on n-type silicon substrate. The band gap values of the p-type porous silicon are always higher than the n-type porous silicon samples. This indicates an active etching process has occurred in p-type silicon during anodization to produce larger micropores at higher porosity.

The thermal diffusivity, carrier diffusion coefficient, surface recombination velocity and recombination lifetime of both p-type and n-type porous silicon layers were determined from the photoacoustic phase signal-frequency dependent using He-Ne laser as the excitation source. The thermal diffusivity (0.0493 - 0.0597) cm<sup>2</sup>/s and diffusion coefficient (3.33 - 4.07) cm<sup>2</sup>/s of porous silicon decrease consistently with the increasing of porosity. The thermal diffusivity (0.0493 - 0.0562) cm<sup>2</sup>/s and diffusion coefficient values (3.33 - 3.83) cm<sup>2</sup>/s of porous silicon prepared on p-type silicon substrates were obtained lower than the porous silicon prepared on n-type silicon substrates ((0.0541 - 0.0597) cm<sup>2</sup>/s and (3.69 - 4.07) cm<sup>2</sup>/s). This could be due to the enhancement of air and oxygen molecules impregnated inside the enlarged micropores with sponge-like spherical morphology that acted as the barriers for thermal diffusion.

The surface recombination velocity of these samples ranges from 314.4 cm/s to 344.0 cm/s, while the recombination lifetime lies in the range from 71.6  $\mu$ s to 97.6  $\mu$ s. The surface recombination velocity of porous silicon increases as the increase of porosity.

The surface recombination velocity of p-type porous silicon (324.1 - 344.0) cm/s is higher than the porous silicon layer prepared on n-type silicon substrates (314.4 - 330.3) cm/s. The XRD, EDX spectra and SEM photographs confirmed that the porous silicon layer remained crystalline and consists of a large network of tiny micropores impregnated with luminescent Si-oxygen bonds.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Doktor Falsafah.

**CIRI-CIRI OPTIK, TERMA DAN PENGANGKUTAN PEMBAWA PADA  
LAPISAN SILIKON BERPOROS DITENTUKAN DENGAN  
MENGGUNAKAN SPEKTROSKOPI FOTOAKUSTIK**

Oleh

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Dalam kajian ini, lapisan silikon berporos dihasilkan di atas silikon jenis p dan jenis n dengan menggunakan cara hakisan elektrokimia pada lima ketumpatan arus yang berbeza (iaitu 16.98, 22.64, 28.29, 33.96 dan 39.62)  $\text{mA/cm}^2$ . Tempoh hakisan ditetapkan pada 20 minit untuk tujuan ini. Dalam siri penyediaan yang kedua, silikon telah dianodisasi pada enam tempoh hakisan yang berbeza (iaitu 20, 25, 30, 35, 40 dan 45) minit dengan ketumpatan arus yang tetap pada  $22.64 \text{ mA/cm}^2$ . Spektra fotopenyinaran, yang telah diukur dengan spectrophotometer optik gentian menunjukkan puncak fotopenyinaran mengalami anjakan-biru ke tenaga yang lebih tinggi dengan penambahan keporosan.

Teknik spektroskopi fotoakustik telah digunakan untuk mengelaskan ciri-ciri optik, terma dan pengangkutan pembawa bagi sampel-sampel ini. Pengukuran ciri-ciri optik telah dilakukan pada tiga frekuensi termodulasi yang berbeza (15 Hz, 23 Hz dan 33 Hz).

Puncak penyerapan menunjukkan anjakan-biru ke tenaga yang lebih tinggi dengan penambahan keporosan. Jurang tenaga silikon berporos ditentukan daripada spektra fotoakustik yang diukur pada 23 Hz dan 33 Hz secara berasingan. Jurang tenaga meningkat secara linear dengan keporosan daripada 1.80 eV ke 2.00 eV untuk silikon berporos yang dihasilkan atas silikon jenis p, dan daripada 1.70 eV ke 1.86 eV bagi silikon berporos yang disediakan atas silikon jenis n. Jurang tenaga silikon berporos jenis p adalah lebih tinggi daripada silikon berporos jenis n. Ini menunjukkan suatu proses hakisan yang aktif telah wujud dalam silikon jenis p semasa anodisasi bagi menghasilkan rongga-rongga yang lebih besar pada keporosan yang lebih tinggi.

Resapan terma, pemalar peresapan pembawa, halaju penggabungan semula pada permukaan dan hayat penggabungan pembawa bagi kedua-dua lapisan silikon berporos jenis p dan n ditentukan daripada hubungan antara isyarat fasa-frekuensi dengan menggunakan He-Ne laser sebagai sumber pengujaan. Resapan terma (0.0493 - 0.0597)  $\text{cm}^2/\text{s}$  dan pemalar peresapan (3.33 - 4.07)  $\text{cm}^2/\text{s}$  silikon berporos berkurangan secara konsisten dengan peningkatan keporosan. Nilai resapan terma (0.0493 - 0.0562)  $\text{cm}^2/\text{s}$  dan pemalar peresapan (3.33 - 3.83)  $\text{cm}^2/\text{s}$  silikon berporos jenis p didapati lebih rendah daripada silikon berporos yang dihasilkan atas silikon jenis n ((0.0541 - 0.0597)  $\text{cm}^2/\text{s}$  dan (3.69 - 4.07)  $\text{cm}^2/\text{s}$ ). Ini boleh disebabkan oleh peningkatan molekul-molekul udara dan oksigen yang terbenam di dalam rongga membesar bermorfologi sfera yang bertindak sebagai penghalang kepada resapan terma.

Halaju penggabungan semula bagi sample-sampel ini berada di antara julat dari 314.4  $\text{cm}/\text{s}$  ke 344.0  $\text{cm}/\text{s}$ , manakala hayat penggabungan berada di dalam julat dari 71.6  $\mu\text{s}$  ke

97.6  $\mu$ s. Halaju penggabungan semula porous silikon bertambah dengan peningkatan keporosan. Silikon berporos jenis p mempunyai halaju penggabungan semula (324.1 - 344.0) cm/s yang lebih tinggi berbanding dengan silikon berporos yang dihasilkan di atas substrat silikon jenis n (314.4 - 330.3) cm/s. Spektra XRD, EDX dan SEM fotograf mengesahkan lapisan silikon berporos mengekalkan struktur hablur yang mengandungi banyak rongga-rongga yang kecil diliputi dengan ikatan silikon dan oksigen berluminar.

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I certify that an Examination Committee has met on 10<sup>th</sup> July 2006 to conduct the final examination of Chan Kok Sheng on his Philosophy of Doctoral thesis entitled “Optical, Thermal and Carrier Transport Properties of Porous Silicon Layer Determined Using Photoacoustic Spectroscopy” in accordance with University Pertanian Malaysia (Higher Degree) Act 1980 and University Pertanian Malaysia (Higher Degree) Regulation 1981. The Committee recommends that the candidate be awarded the relevant degree. Members of the Examination Committee are as follows:

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## **DECLARATION**

I hereby declare that the thesis is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at UPM or other institutions.

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**CHAN KOK SHENG**

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