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Photocurrent of nanoassembled Si film in contact with electrolyte

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Abstract

Nanoassembled Si thin films on conducting glass have been prepared. Films are photoactive and demonstrate "n-type" behavior in contact with electrolyte. Good correlation has been found between band gap obtained from luminescence and photocurrent. Up to such a small particle sizes the Si is still indirect optical material. Si nanoparticles demonstrate significantly reduced electron affinity 2.4 eV with much higher position of the bottom of conducting band compared to bulk Si while position of valence band did not change.

Keywords: Thin films; Electrode materials; Electronic band structure; Luminescence; Photocurrent

1. Introduction

Porous Si is a material of interest because of fundamental physical properties of quantum sized objects and possible promising applications in Si-based industry. Nanosized crystallites (<5 nm) have electrical and optical properties which are different from the bulk Si. Large specific surface area, increased band gap, luminescence in the visible region, changed electronic structure are basic properties used to design different devices such as solar cells with antireflecting coating [1], gas sensors, cold cathodes, flat panels, super capacitors, etc. [2,3]. It has also been proposed to use porous Si to improve hydrogen generation by p-Si in photoelectrolyses [4].

The usual way is to study porous Si on the Si wafer used for preparation. Unfortunately, in many cases, it is difficult to separate the properties of highly resistive, some times very thin layer of nanosized Si from the bulk material. The purpose of this report is to show a simple way to examine optical and photoelectrochemical properties of nanosized Si without influence of bulk Si. Prepared porous Si was separated from Si wafer and deposited as film on different substrate (conducting glass).

2. Experimental

Si nanoparticles were made by anodic etching of 0.12 Ω cm (1 0 0) p-type Si wafer with following dispersion of particles in toluen:ethanol (2:1) mixture by ultrasonic bath. The piece of Si wafer of rectangular form with 2 cm width was immersed into electrolyte on depth of 5 mm. Anodic current was about 40 mA/cm^2 and processing time was 15 min. HF (46%):H_2O_2 (30%):methanol (97%) 3:3:1 mixture was used as electrolyte. After anodization and before ultrasonic bath, the porous Si was carefully rinsed by methanol. Films were prepared by electrophoretic deposition [6] of Si nanoparticles on conducting glass from suspension. Deposited films were calcinated at 150 °C in N_2 atmosphere. As prepared films have yellow color and demonstrate interference maxima and minima during transmittance measurements suggesting films uniformity. The thickness measured by SEM was about 1 μm (Fig. 1). Spectra of luminescence have been measured by Jusco FP-750 spectrofluorometer. Photoelectrochemical measurements were carried out in 0.1 M H_2SO_4 electrolyte. CHI440 potentiostat and three-electrode cell was used to record photocurrent. All potentials are versus Ag/$AgCl_2$ reference electrode. Thousand Watts Xenon lamp with monochromator was used as source of white and monochromatic light. Actual white light intensity was 60 mW/cm^2.

3. Results and discussion

Freshly prepared (dispersed in toluene:ethanol) Si nanoparticles show luminescence with peak at 2.28 eV (545 nm, Fig. 2). From luminescence maximum, the particle size can be estimated to be around ∼2 nm [5]. Excitation spectrum (dashed curve in Fig. 2.) is proportional to absorption and can be used to estimate optical band gap which is about 2.5 eV.

Photoelectrochemical properties of films have been studied in 0.1 M H_2SO_4 electrolyte using three-electrode cell. Working electrode demonstrates different potentials in darkness and under white light (Fig. 3) at the open circuit conditions. This photovoltage is about 0.5 V and shows "n-type" behavior. It suggests more than 0.5 V band bending at the equilibrium. The polarity of the voltage says that photogenerated electrons go to substrate

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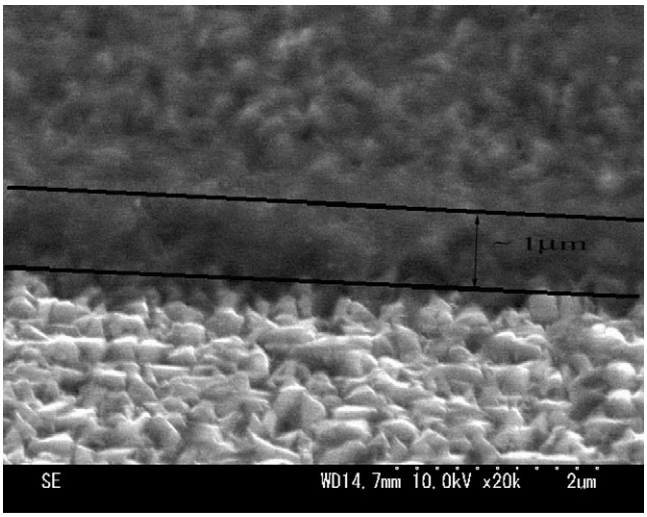

Fig. 1. SEM image of scratched and tilted sample. Si film thickness is about 1 μm.

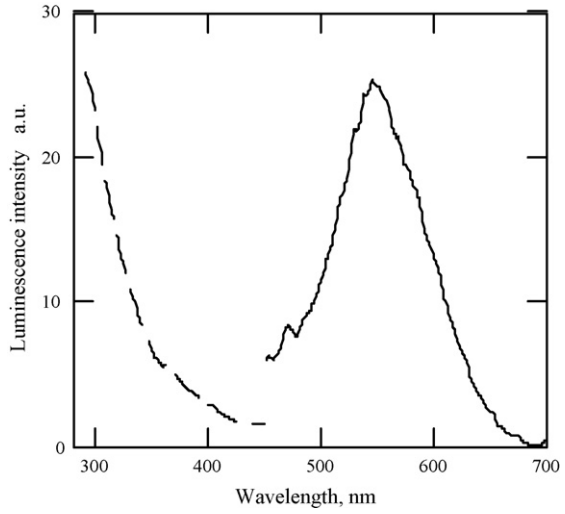

Fig. 2. Emission spectra (solid curve) and excitation (dashed curve) of luminescence of freshly prepared Si nanoparticles in toluene/ethanol mixture.

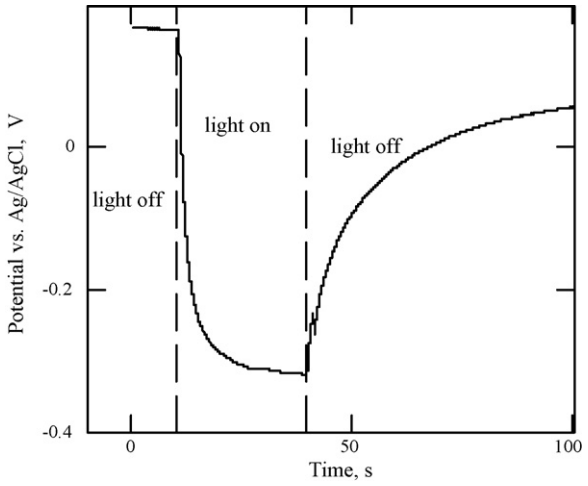

Fig. 3. Photopotential of sample vs. $Ag/AgCl_2$ reference electrode measured in 0.1 M H_2SO_4 electrolyte.

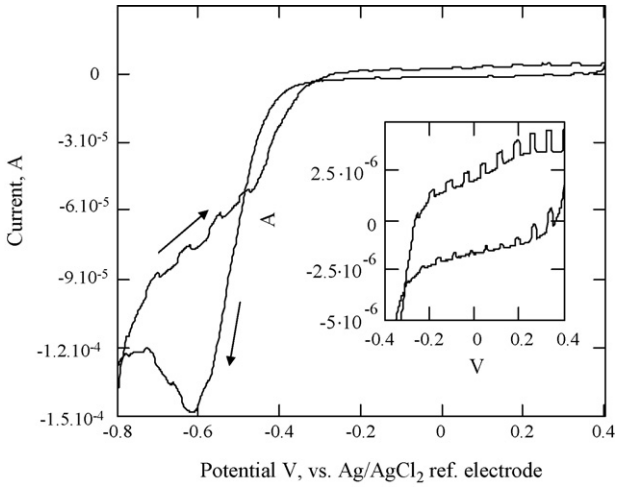

Fig. 4. Cyclic voltammetry under chopped white light of 60 mW/cm^2 intensity. The inset shows enlarged region of small current.

and holes go to contact with electrolyte. So, originally p-type Si was converted to n-type Si nanoparticles. This is in the agreement with high internal resistance of porous Si [2].

Cyclic voltammetry (Fig. 4) measured under chopped light allows to measure photo and dark current simultaneously. Significant dark current at negative potentials was present caused by reaction between substrate (fluorine doped SnO_2) and electrolyte. After dark current subtraction, the photocurrent (Fig. 5) shows three significant regions. The first is from 0.4 to −0.2 V. It increases from negative to positive potential with increasing of electric field in nanoparticles helping to separate photogenerated charge. This photocurrent is relatively small due to lack of hole scavenging at contact with electrolyte. Probably, the main holes consumer is oxidation reaction of Si. Second region is from −0.6 to −0.2 V. The photocurrent significantly increases due to increasing of reaction probability between generated holes and hydrogen. Third region is from −0.6 to negative side of potential. The photocurrent decreases with decreasing of electric field inside of Si particle at more negative potentials and riches zero at

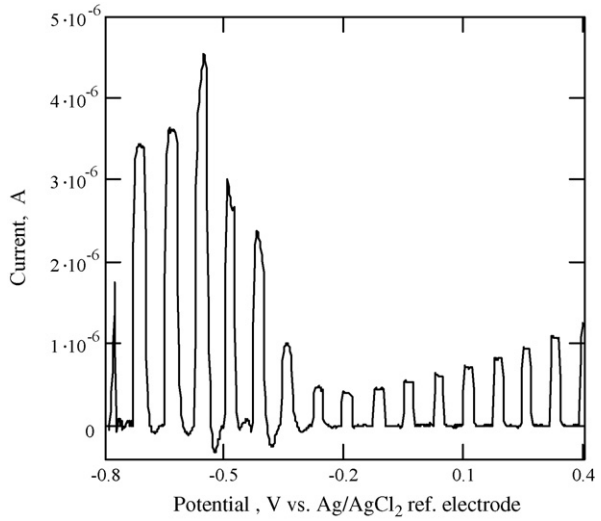

Fig. 5. Photocurrent of Si nanoparticles vs. applied potential.

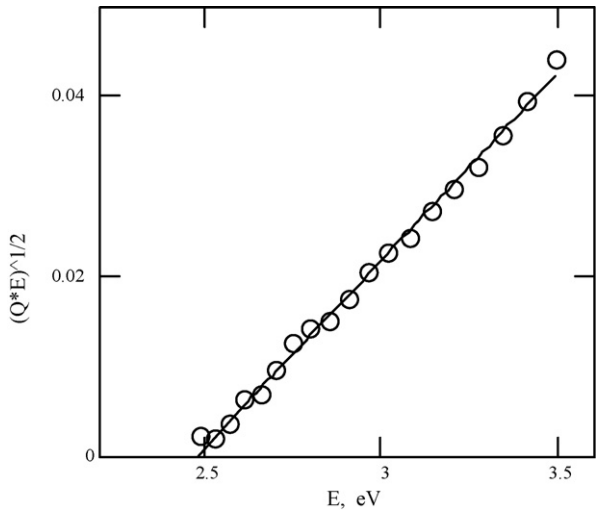

Fig. 6. Spectral dependence of quantum yield (Q) vs. photon energy. Special scale was applied to show indirect optical transitions. Measured optical band gap is 2.5 eV.

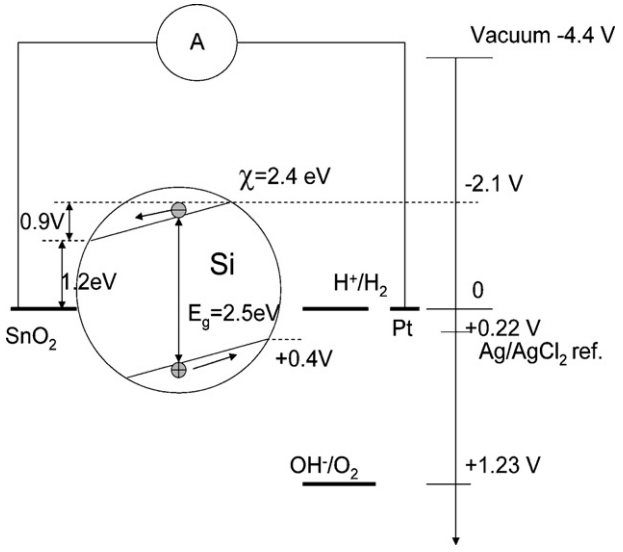

Fig. 7. Bands positions for Si nanoparticles in contact with electrolyte.

flat bands. Estimated flat band potential is about −0.9 V versus $Ag/AgCl_2$ reference electrode.

Spectral dependence of photocurrent was recorded at fixed applied bias (+0.2 V) where short circuit condition is performed. Behavior of the photocurrent quantum yield (Q) versus photon energy (Fig. 6) demonstrates indirect band gap 2.48 eV. This is much higher than band gap of bulk Si (1.12 eV) due to quantum size effect.

On the basis of obtained band gap (2.48 eV) and flat band potential (−0.9 V) it is possible now to estimate the electron affinity χ and band positions of nanosized Si (Fig. 7). Taking into account the low concentrations of free carriers due to trap by surface states [2], the Fermi level is fixed at the middle of band gap. Summarizing, the flat band potential (−0.9 V) and distance between Fermi level and bottom of conduction band (−1.25 V), the position of conduction band against $Ag/AgCl_2$ is found to be −2.15 V. Valence band position can be found by subtracting the value of band gap (2.5 eV) and it is +0.35 V. Electron affinity as distance between bottom of conduction band and vacuum level can be found using potential of $Ag/AgCl_2$ in vacuum scale (+4.6 eV) and it is ∼2.4 eV. This is significantly lower then for bulk Si (3.8 eV). It is interesting to mention that valence band position of bulk Si (+0.4 versus $Ag/AgCl_2$) is almost the same as in the case of nanosized Si.

4. Conclusions

Nanoassembled Si films on conducting glass are photoactive and demonstrate “n-type” behavior. Good correlation has been found between band gap obtained from luminescence and photocurrent. Up to such a small particle sizes, the Si is still an indirect optical material. Si nanoparticles demonstrate significantly reduced electron affinity 2.4 eV with much higher position of the bottom of conducting band compared to bulk Si while position of valence band did not change.

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