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ScienceDirect
Applied Surface Science 253 (2007) 4566–4569
applied surface science
www.elsevier.com/locate/apsusc

Study of photoconductivity and photoluminescence of organic/porous silicon complexes

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Received 17 May 2006; received in revised form 25 September 2006; accepted 8 October 2006
Available online 13 November 2006

Abstract

In this paper, time-varying photoconductivity (PC) and the photoluminescence (PL) of different complexes were studied. Due to thick polymer layer hindering light penetrating into porous silicon (PS) layer, intrinsic PS luminescence in polymer/PS system disappeared. The physical origin of PL may be related to the recombination mechanisms involving surface defect states such as silicon oxide, siloxene. Due to carrier transfer controlled by different energy barrier, different devices prepared from different doped Si wafer showed opposite current–voltage characteristic.

Keywords: Porous silicon; Complexes; Photoconductivity; Photoluminescence

1. Introduction

The discovery of room temperature visible photoluminescence (PL) from PS prepared in hydrofluoric acid has stimulated a great of interest in recent years because of its potential application in solar cells, light emitting diodes, optical sensors, moisture detector, interference filters, waveguide, SOI structures, and biomedical applications, etc. [1]. But up to now, the nature of porous silicon (PS) luminescence has not yet been confirmed. The photoconductivity (PC) is an important tool for the study of photo-generated carriers transfer in PS and also gives an insight into recombination mechanism. The PS luminescence is controlled by the radiative combination process, but the PC mainly is controlled by irradiative combination process, which can give complimentary information for understanding of carriers transfer and origin of PS luminescence. Many papers were published to study the relationship between PC and PL spectroscopy [2–9]. Some author considered that the transition states in PS are consistent of a series of energy levels and surface states formed in hydrogen-rich layer and SiO_X, which produced PS luminescence. Mehra researched the influence of etching parameters on PC spectra of PS. They found that the optical activity of PS is based on quantum effect in nano-crystalline with disorder electronic boundaries with the surface states, and combination process in PS is found to have contribution from both monomolecular and bimolecular processes. Other author found that time evolution of PC indicated the presence of two competing mechanisms, one is related to photo-induced creation of charge carriers in silicon substrate followed by diffusion into PS layer, and the other is associated to removing of hydrogen from PS.

Furthermore, in previous articles, several research groups have investigated the optical properties of complexes made by PS layer capped with organic materials [10–18] to increase efficiency and carrier injection of PS based devices. Rendu researched the PS/poly (*p*-phenylene vinylene) (PPV) system and found that there is no interaction between both components and an energy transfer from PS to PPV is generated. A light emitting diode made by contacting an n-type PS film with chemically polymerized polyaniline showed a rectifying *I*–*V* characteristic and emitted red light under a forward bias voltage exceeding 3 V. The addition of the polymer layer into PS devices, which have been fabricated from n-type Si substrates using indium tin oxide, hole transporting poly (9-vinyl carbazole) and p-type nickel oxide film as hole injecting

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doi:10.1016/j.apsusc.2006.10.007

contacts, led to an increase in device quantum efficiency of two orders of magnitude.

In our paper, the complexes made by PS capped with PPV or Alq_3 were investigated. The influence of doping level on PC and PL of PS-based devices were obtained. Furthermore, SEM observations were carried out in this article.

2. Experiments

PS films prepared by electrochemically etched use two type silicon substrates: one is (1 0 0) n-type silicon wafer with a resistivity of 1–10 Ω cm, the other is (1 0 0) n-type epitaxial silicon (ESi) wafer with resistivities of 0.01–0.03 Ω cm for epitaxial layer and 1–10 Ω cm for bulk layer. The Si wafers were first cleaned using aqueous HF acid for 10 s to remove natural oxide film on Si surface. The back sides of Si wafers were coated with an aluminum layer and then were annealed at 400 °C for 4 min to provide a low resistance ohmic electric contact. The resulting Si wafers were electrochemically etched under a constant density of 30 mA/cm^2 in a HF-ethanol (1:2 in volume) mixed solution for 1 min. During electrochemical etching, the wafers were illuminated by a 50 W tungsten lamp to produce holes. After etching, PS were rinsed with de-ionized water and dried in air. Before the polymer was spun onto PS, PS samples were dipped in aqueous HF to remove any native oxide and survival aluminum film on PS surface. The polymer solution was spun at 1000 rpm for 6 s and then at 3000 rmp for 30 s and then PS samples were subsequently baked at 100 °C for 30 min. A typical polymer formulation used is 10 mg poly (*N*-vinylcarbazole) (PVK) or 8-hydroxyquinoline aluminum (Alq_3) in 10 ml tetrahydrofuran.

The samples were characterized by PL spectroscopy, PC spectroscopy and scanning electron microscopy (SEM). The PL spectra excited by a 360 nm wavelength laser were measured using a HITACHI F-4500 fluorescence spectrophotometer. The PC measurements were carried out using a computer-interfaced KEITHLEY 4200 semiconductor characteristics system. The morphology observations were carried out using a FEI SIRION FESEM. All the measurements were carried out at room temperature.

3. Results and discussions

Fig. 1 showed the PL spectra of polymer/PS system, in which PS was prepared from general Si (GPS) and from ESi (EPS). Furthermore, intrinsic PL spectra of polymer were also shown in Fig. 1c. From Fig. 1c, it can found the Alq_3 peak was centered at 498 nm and the PL spectrum of PVK has a peak centered at 427 nm. It can be seen that PL spectrum of the as-prepared PS prepared from both Si wafers exhibits a broad multiple peak from 420 to 470 nm and PL efficiency of GPS is higher than that of EPS. It was well known that PS luminescence is strongly depended on morphology and large specific surface of PS.

Fig. 2 showed SEM images of surface morphology of GPS (Fig. 2a) and EPS (Fig. 2b). GPS porosity is higher than that of EPS, which led to stronger blue emission of GPS, as shown in Fig. 1. In addition, from the frequencies of Raman peak, the quantum size effects cannot be observed in both PS films. It was indicated that PL luminescence in blue band might come from the defects states on the surface of silicon rods and in the Si complexes including siloxene, Si oxide and Si hydrides [19]. In Ref. [11], authors researched PL of PPV/PS system and found PL spectrum of PS/PPV system showed all characteristics of the components with, in addition, a band located at 473 nm, which assumed to be related to the energy transfer from PS to PPV. But in Ref. [16], it was found that there is no interaction between PPV and PS, which also was proved by FTIR spectra and Raman measurements. Furthermore, PL spectrum of PS exhibited a peak at 620 nm while that of PPV has a broad multiple-peak structure between 510 and 550 nm. In our experiment, after the polymer was spun on PS surface, PL spectra of PS/polymer complexes only showed the characteristic of the polymer, as showed in Fig. 1a and b. In Ref. [19], the authors have reported that the PL spectra of PS/polymer complexes were strongly affected by the thickness of polymer.

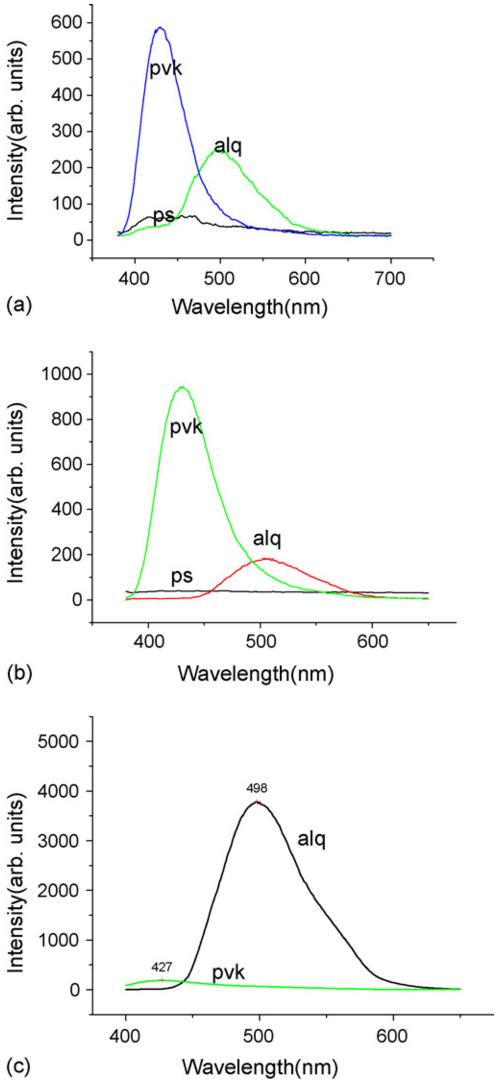

Fig. 1. PL spectra of polymers (c) and polymer/PS complexes prepared from general Si (a) or ESE (b).