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Formation of photoluminescent n-type macroporous silicon: Effect of magnetic field and lateral electric potential

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ABSTRACT

Metal electrode-free electrochemical etching of low doped n-type silicon substrates, under the combined effect of magnetic and lateral electric field, is used to fabricate photoluminescent n-type porous silicon structures in dark conditions. A lateral gradient in terms of structural characteristics (*i.e.* thickness and pore dimensions) along the electric field direction is formed. Enhancement of electric and magnetic field resulted in the increase of pore density and a change in the shape of the macropore structure, from circular to square morphology. Broad photoluminescence (PL) emission from 500 to 800 nm, with a PL peak wavelength ranging from 571 to 642 nm, is attributed to the wide range of microporous features present on the porous silicon layer.

1. Introduction

Porous silicon (PSi) has been extensively studied since the discovery of its photoluminescence (PL) at room temperature [1]. However, most of the applications involving photoluminescent PSi microstructures are fabricated using p-type silicon, while for applications in microelectronics and light-emitting diode technology n-type silicon is more desirable [2,3]. It is well known [4,5] that the structural characteristics of PSi fabricated with p-type and n-type silicon are completely different. Electrochemical anodisation using a HF (hydrofluoric acid) based electrolyte is the most commonly used technique for the fabrication of PSi. In order to carry out an anodic dissolution at the HF-silicon interface and consequently PSi formation, the presence of valance band holes is required to assist the electrochemical reaction. For p-type silicon, the majority charge carriers are holes, and etching process is not limited by their availability, so p-type porous silicon (p-PSi) layers are easily produced. On the other hand, light-assisted anodisation (*i.e.* photo-generation of holes) is a conventional technique for obtaining n-type porous silicon (n-PSi) [6–8]. Nevertheless, light-assisted etching is a depth limited process.

In 2006, Lin et al., [3] proposed an alternative method (*i.e.* using Hall effect) to fabricate photoluminescent structures from n-type silicon under dark conditions (illumination-free) which involves the application of perpendicular electric and magnetic fields, to drive holes towards the HF-silicon interface. Sample displaying a considerable amount of gradient in thickness and slight variation in PL peak and intensity, along the electric field (EF) direction was studied as a function of magnetic field (0–20 mT). Many groups have shown that graded PSi films can promote cell adhesion, viability and act as sensors with the required element infiltrating inside the pores (proteins, enzymes, cells, *etc.*) [9–12]. Nevertheless, the aforementioned PSi structures are limited by their pore dimensions, *i.e.,* only elements smaller than the pore size can be detected, which suggests the requirement of pores with higher dimensions (macropores) for biosensing applications. Conventionally, macropore formation in low doped n-type Si, using HF-containing electrolytes with strong oxidizers [13,14], has been reported. Li et al., [2], on the other hand, reported macropore formation through electrode-assisted lateral electrical field, to produce photoluminescent n-PSi. Magnetic field-assisted (>1 T) anodisation had been recently utilized in order to enhance the light-emission (PL) properties and for the achievement of highly directional etching in n-type silicon substrates [15–18].

In spite of the above mentioned works on the electric/magnetic field assisted macropore formation in n-type Si, the effect of both fabrication parameters on the structural and optical characteristics has not been further explored. In this work, we report the effect of electric/magnetic field on pore morphology and optical properties of n-PSi structures. By using a combined effect of magnetic and lateral electrical field during the etching process, we demonstrate the formation of different macropore morphologies (circular and square) and light-emission properties. Unlike the previous reports [3] which have been only focused on the appearance of the gradient,

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we explore the possibility of tuning the morphology and dimension of the pores, as well as the porosity in the n-PSi structures by the enhancement of the electric/magnetic field applied during the fabrication process. A part from that, we obtained a structural graded sample (in terms of thickness and pore size) without performing an asymmetric electrochemical anodisation [9–12] since it is the most commonly used technique for fabricating graded samples.

2. Experimental details

Schematic diagram of the experimental setup used to form electrochemically PSi, using low doped, ⟨1 0 0⟩ oriented n-type silicon substrates with an electric resistivity of 8–12 Ω cm (dopant concentration ~ $10^{14}/\text{cm}^3$) is shown in Fig. 1(a). Samples were fabricated under the influence of electric and magnetic field simultaneously. A lateral potential (V_x) is biased across two electrodes (anode/cathode) made by rubbing Ga–In eutectic onto the backside of the wafer at the two ends of an n-type silicon substrate (15 mm × 30 mm), giving rise to the flow of current I_x. A magnetic field (B_y) is placed perpendicular to the EF direction, so that majority charge carriers (electrons, e^-) flowing in the x-direction will be swept down by the effect of the resulting Lorentz force ($\vec{F}_z = q\vec{v}_x \times \vec{B}_y$), as indicated in schematic of Fig. 1(b). Generation of holes at the effective area of the substrate exposed to the HF based electrolyte (*i.e.* HF-silicon interface) promotes the reaction. An increased magnetic field density leads to a major accumulation of valence band holes at the HF-silicon interface while on the other hand a large potential supplied will contribute to the formation of a structural gradient in the supply of holes along the EF direction.

A mixture of 48 wt% aqueous HF and 99.7 vol% ethanol in volumetric ratio of 1:4 was used as electrolyte to perform the etching process for 10 min, at room temperature. The main body of the HF electrolyte container is a cell made of Teflon. No second metal-electrode is needed in our experimental setup, opening the possibility of the design of a hermetic etching HF electrolyte container (illumination-free). Besides, the metal-electrode contamination can be prevented.

Two samples were fabricated to show the effect of electric/magnetic field on pore morphology and optical properties. Sample S1 was fabricated by applying a lateral voltage of 15 V and a perpendicular magnetic field of 20 mT, whilst for sample S2, 30 V and 40 mT were supplied in the fabrication process, respectively. The morphologies of the etched pores (top and cross sectional views) were observed using a field-emission scanning electron microscope (FESEM, Hitachi S-5500). The PL measurements on freshly etched n-PSi samples were perform using an excitation wavelength of 250 nm from a Xenon lamp (Cary Eclipse Spectrophotometer) at different locations across the EF direction for qualitative comparison.

3. Results and discussion

Four different locations (A to D; Figs. 2 and 3a) on the PSi samples were considered for the FESEM micrographs as well as for the PL measurements in order to investigate the change in the structural and optical properties of PSi (structural gradient), along the EF direction for samples S1 and S2. Location A is closer to the cathode of the substrate while location D is the closer to the anode as shown in Figs. 2 and 3a. Since lateral potential is applied across the Si wafer, in the present experimental configuration, the two ends of the silicon substrate play the role of anode and cathode, without the necessity of a second metal-electrode. Thus, the electrochemical reaction takes place with a flow of current I_x (conventional current) from the positive end/anode of the silicon substrate (resistivity of 8–12 Ω cm), to the negative end/cathode, through relatively more conductive electrolyte (path of least resistance) *i.e.* forming a current loop through the electrolyte.

Cross section and top views taken at four different locations (A–D, Fig. 2a) of sample S1 are presented in Fig. 2b–g. Although location A (near cathode, ref. to Fig. 2a) of the porous sample shows no apparent pore formation through the naked eye, the formation of a thin film composed of microporous features is revealed through FESEM micrograph (Fig. 2b). Thickness of the porous layer (cross section) in this region was not measurable through FESEM. Thus, location A corresponds to a region on the substrate 2 mm away from the extreme end of the cathodic region in contact with the electrolyte. No porous silicon formation (surface or cross-sections) beyond location A (towards the extreme end of cathodic region) was observed through FESEM. Images corresponding to locations B (Fig. 2c and d) and C (Fig. 2e and f) clearly exhibit the formation of a relatively thicker (approx. from 82 to 98 nm) porous layer containing micro-, meso- and macropore features. The formation of structural gradient in terms of thickness and pore size along the EF direction is demonstrated in the form of increased thickness and pore dimensions towards anode. Cross sectional view taken at location D (Fig. 2g), *i.e.* the location at 2 mm away from the extreme end of the anodic region in contact with the electrolyte shows the formation of large

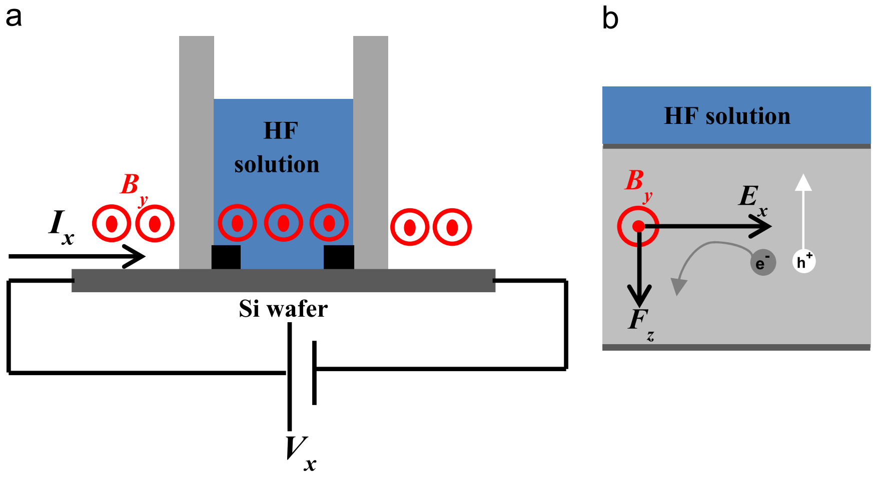

Fig. 1. (a) Schematic diagram of the experimental setup used for the fabrication of n-PSi samples. (b) Schematic showing the effect of magnetic field at the HF-silicon interface on n-type substrates during electrochemical etching.