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Blue luminescence from porous layers produced by metal-assisted chemical etching on low-doped silicon

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Abstract

Photoluminescent porous layers were formed on highly resistive p-type silicon by a metal-assisted chemical etching method using $K_2Cr_2O_7$ as an oxidizing agent. A thin layer of Ag is deposited on the (1 0 0) Si surface prior to immersion in a solution of HF and $K_2Cr_2O_7$. The morphology of the porous silicon (PS) layer formed by this method as a function of etching time was investigated by scanning electron microscopy (SEM). It shows that the surface is formed by macropores filled with microporous silicon. The porous layers were characterized by backscattering spectrometry (BS) as a function of etching time in random and channelling mode. Channelling spectra show that the porous layer remains crystalline after etching. On the other hand, random and channelling spectra show that the deposited silver diffuses into the pore. Luminescence from metal-assisted chemically etched layers was measured. It was found that the PL intensity increases with increasing etching time. This behaviour is attributed to increase of the density of the silicon nanostructure. Finally, the PL spectra show two peaks of emission at 450 and 600 nm.

Keywords: Porous silicon; Photoluminescence; Metal-assisted chemical etching

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1. Introduction

Light-emitting materials on a porous silicon wafer have a great potential for use in optoelectronic industries. Porous silicon for light-emitting layers on a Si substrate is commonly formed by anodic (electrochemical) etching in HF-based solutions [1,2]. Recently, a new method, termed metal-assisted chemical etching, has been developed, which is relatively simple compared to the anodization method. It needs no electrodes on the back surface of Si wafers and enables formation of uniform porous silicon layers [3–5]. A thin metallic

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film (Au, Pt, Al, Pd, etc.) is generally deposited directly on a silicon surface prior to immersion in an etchant composed of HF and an oxidizing agent. In our previous studies, we have used this method on highly resistive Si samples; we have demonstrated that Pd-assisted chemical etching allows the formation of a thick nanoporous layer on highly resistive silicon [6]. Moreover, we have formed visible-light-emitting layers on highly resistive p-type silicon using $Na_2S_2O_8$ as an oxidizing agent and silver (Ag) as the deposited metal [7]. The etched layers exhibit strong red luminescence with a photoluminescence (PL) peak centred at 655 nm.

The colour of visible light emission from PS is generally red or yellow, and the blue or green light emission from PS has been studied in order to develop display devices. Generally, the blue luminescence is obtained after etching and after dipping in ethanol/H_2O solution for a long time (170 h) or chemical oxidation [8,9].

In this paper, we report on the formation of blue-light-emitting layers on highly resistive p-type silicon using $K_2Cr_2O_7$ as an oxidizing agent and Ag as deposited metal without post-etching treatment. We discuss the etching time dependence on the morphology of porous silicon layers and the PL peak intensity. The morphology of porous silicon layers was examined by SEM and backscattering spectrometry (BS). The latter shows also the behaviour of deposited silver as a function of etching time. The changes in the PL spectrum are attributed to the structural modifications of porous silicon layers caused by etching.

2. Experimental procedure

The metal-assisted chemical etching processes were applied to p-type Si wafers Czochralski-grown (1 0 0) 100 Ω cm. Thin silver films of about 20 nm are evaporated under vacuum ($\sim 10^{-5}$ mbar) conditions onto the silicon samples. The etchant solution used is 22.5 M HF-0.05 M $K_2Cr_2O_7$–H_2O. After etching the samples are rinsed with deionised water. The etching is performed at room temperature. The time of etching is varied between 30 s and 20 min.

For the SEM measurements, a Philips XL 30 microscope was used. The RBS analyses were performed with a 2 MeV He^+ beam provided by the 3.75 MeV Van de Graaf accelerator at CRNA (Algiers). The detector was installed at a scattering angle of 165° in Cornell geometry and had a solid angle of 2.5 msr. The energy resolution of the detecting system was 18 keV. The beam current was collimated by two apertures of $0.5 \times 0.5\,mm^2$ cross-section placed 1500 mm apart for a maximum beam divergence of 0.04°. PL from the Ag-assisted chemically etched silicon was measured under He–Cd laser excitation (325 nm), in vacuum ($<10^{-2}$ Torr), by a monochromator and photomultiplier tube.

3. Results and discussion

Fig. 1a displays a plan view SEM image of a p-Si (1 0 0) sample (100 Ω cm), which was subjected to Ag-assisted chemical etching in 22.5 M HF-0.05 M $K_2Cr_2O_7$–H_2O solution for 30 s. It shows that the surface is dominated by a high density of channels (macropores) of about 100 nm diameter that penetrate into the bulk of the silicon. The increase of the etching time to 10 min induces an increase of both macropore density and pore diameter. The later reach a value of 150 nm, Fig. 1b. The cross-sectional SEM views (Figs. 2a and 2b) of the samples etched during 30 s and 20 min, respectively show that the etching progresses in an anisotropic manner. The macropores have a conical form for an etching time of 30 s, behaviour similar to that recently observed on medium n-type silicon photochemically etched in a HF-ethanoic solution [10], then reach a steady state and become cylindrical for an etching time of about 20 min. The macropores grow parallel and perpendicular to the surface, a result similar to that generally observed on p-type highly resistive silicon electrochemically etched [11]. However this morphology is quite different from that observed on metal-assisted chemically etched PS obtained on high-resistivity silicon with 22.5 M HF-0.05 M $Na_2S_2O_8$–H_2O solution [6]. Indeed, in the latter case, it shows the presence of macropores propagating into the bulk from the surface with no