Doping-induced selective area photoluminescence in porous silicon

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The incubation time (t_i) for the onset of porous Si formation by stain etching in HF:HNO$_3$:H$_2$O was observed to be a strong function of dopant type and concentration. For B-doped *p*-Si, t_i increased significantly with substrate resistivity (ρ), from ~0.5 min for 0.004 Ω cm to ~9 min for 50 Ω cm. P-doped *n*-Si substrates exhibited a t_i which decreased with increasing ρ, from ~10 min for 0.15 Ω cm to ~8 min for 20 Ω cm. We have utilized the difference in t_i between *n*- and *p*-type Si to produce selective area photoluminescence (PL) by Ga$^+$ focused ion beam (FIB) implantation doping and B$^+$ broad beam implantation doping of *n*-type Si. Using 30 kV FIB Ga$^+$ implantation, PL patterns with submicrometer resolution have been obtained for the first time.

Recent reports[1,2] have indicated that porous Si (PoSi) produces a surprising photoluminescence (PL) under ultraviolet (UV) and blue-green wavelength laser excitation. The PL, observable at 300 K with the naked eye, is orange-red in color, corresponding to energies (~1.75–2.00 eV) considerably greater than the band gap of crystalline Si (1.1 eV). In order to obtain optoelectronic devices based on this effect, one needs to fabricate photoemissive porous Si regions of well-defined dimensions with acceptable lithographic resolution. We have previously reported[3] on the fabrication of nanostructures in crystalline Si using focused ion beam (FIB) implantation followed by selective and crystallographically anisotropic chemical etching. In that process, the FIB-implanted region has an extremely low etch rate in KOH solutions. We have subsequently observed that, if instead of KOH a PoSi etch is used, the onset of PoSi formation can be significantly different in the implanted and unimplanted regions. This observation has led us to study the effect of Si doping on the formation of PoSi and its PL properties.

We have used *p*- and *n*-type ⟨100⟩ Si wafers with resistivity (ρ) ranging from 4×10^{-3} to 50 Ω cm. The PoSi was formed by purely chemical ("stain") etching[4–6] at room temperature in a solution of HF : HNO$_3$: H$_2$O in the ratio of 1 : 3 : 5 by volume. The stain-etching technique was used instead of anodization because of its simplicity and the uniformity of resulting PoSi layers. We have measured the incubation time delay (t_i) which occurs[5] between the insertion of the Si into the etching solution and the onset of PoSi production. t_i was obtained for a variety of samples stain etched under two conditions: (a) in normal "white" light ambient, the reflected color of the sample surface was monitored and the time at which the first change from metallic silver-gray to red-brown occurred was noted; (b) under UV (at 365 nm) illumination only, the time for first visible PL observation was noted. As shown in Fig. 1, t_i was found to depend on doping type and concentration. The same general trend is obtained for both illumination conditions. Since all implantation experiments used stain etching under white light ambient, we will restrict our quantitative discussion to t_i results obtained under this condition. The t_i for B-doped Si was generally smaller than for P-doped Si. The difference was increasingly pronounced for more heavily doped samples. For *p*-Si, t_i increased significantly with ρ, from ~0.5 min for 0.0043 Ω cm to ~9 min for 50 Ω cm. In contrast, *n*-Si substrates exhibited a weakly decreasing t_i with increasing ρ, from ~10 min for 0.13 Ω cm to ~8 min for ~20 Ω cm. The values given in Fig. 1 represent averages over several samples at each data point. Occasionally, significant departures from the average t_i value was observed. The p^{++} samples, however, always exhibited a very reproducible t_i of ⩽30 s. This effect is consistent with the basic Si etching mechanism[7,8] which is initiated by the reaction of holes with Si atoms at the etching surface.

PL measurements were performed with a filtered Hg source containing UV peaks at 370–380 nm. Typical photoemissive spectra are shown in Fig. 2(a) for several Si substrates etched for t_i plus 2 min: 0.004 Ω cm p^{++}-Si; 5 Ω cm *p*-Si; 3.2 Ω cm *n*-Si; 10 kV Ga$^+$ FIB-implanted *n*-Si. The PL spectrum for the p^{++} sample exhibits a symmetric signal in a broad band with a peak and full width at half maximum (FWHM) of 660 (1.9 eV) and 133 nm, respectively. The other spectra have the major peak at 630 nm (1.95 eV). The minor peaks at 710 nm (1.75 eV) and at ~530–550 nm (2.3 eV) observed occasionally (from nonuniform areas) are due to contributions from the Hg source reflected by the nonetched Si surface. As shown in Fig. 2(b), the PL spectrum of the p^{++} sample taken after

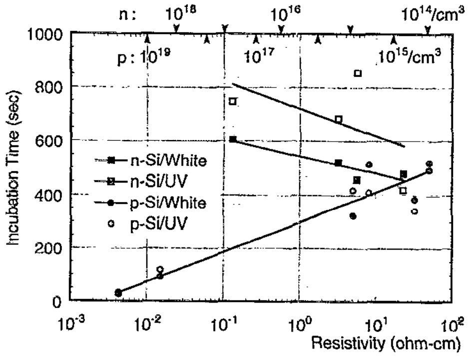

FIG. 1. Incubation time as a function of Si *n*- and *p*-type resistivity.

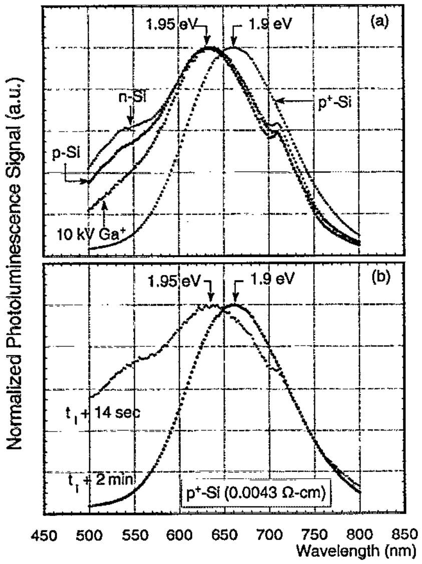

FIG. 2. Photoluminescence spectra of porous Si on (a) n- and p-type substrates stain etched for t_i plus 2 min: 0.0043 Ω cm p-Si; 50 Ω cm p-Si; 3.2 Ω cm n-Si; 10 kV FIB Ga^+ $10^{15}/cm^2$ into 0.1 Ω cm n-Si; (b) 0.0043 Ω cm p-Si for 14 and 120 s past t_i

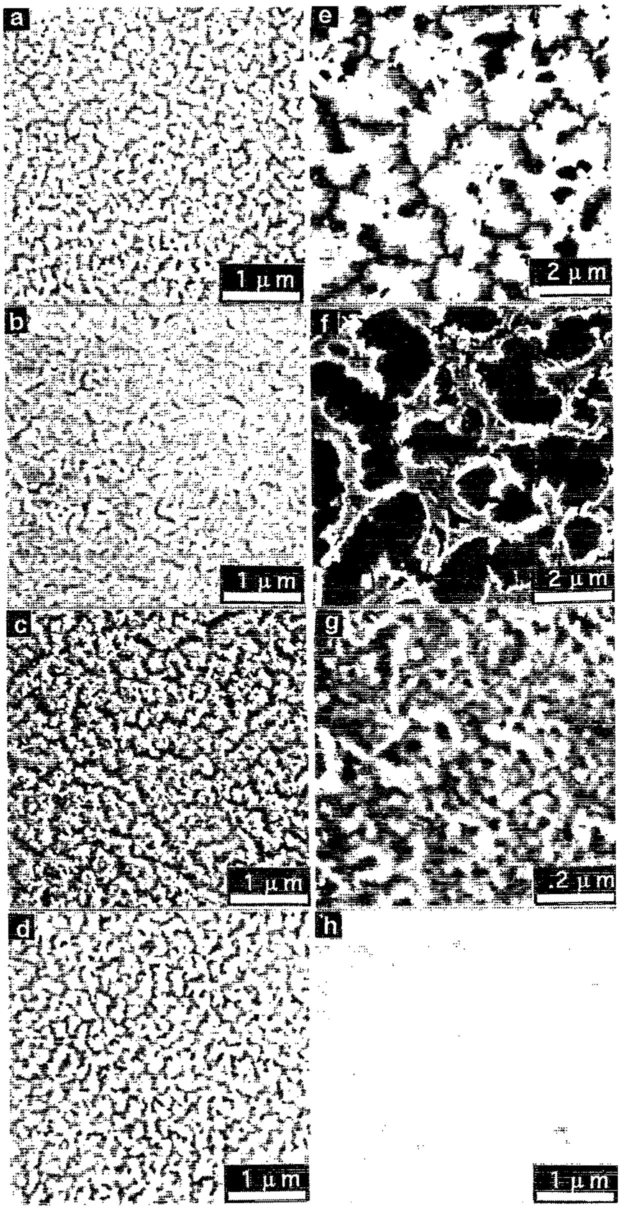

FIG. 3. Surface morphology of porous Si regions stain etched for t_i plus ~2 min on various substrates: (a) 0.13 Ω cm n-Si; (b) 3.2 Ω cm n-Si; (c) 50 Ω cm p-Si; (d) 5Ω cm p-Si; (e) 0.015 Ω cm p-Si; (f) 0.0043 Ω cm p-Si; (g) 0.0043 Ω cm p-Si stain etched for t_i plus ~14 s; (h) 10 kV FIB Ga^+ $10^{15}/cm^2$ into n-Si for t_i plus ~1 min.

only 14 s past t_i also exhibits these additional features, which generally disappear if the process is continued for 2 min. The major peak at 1.9–1.95 eV is consistent with other reports[5,6] of PL from stain-etched porous Si.

The surface morphologies of PoSi on substrates with various ρ values formed after stain etching for 2 min past t_i are shown in Figs. 3(a)–3(f) for 0.13 and 3.2 Ω cm n-Si, and for 50, 5, 0.015, and 0.004 Ω cm p-Si. The n-Si samples exhibit only a minor degree of porosity. The p-Si samples show an increasing porosity level with decreasing ρ. The 0.004 Ω cm p-Si sample stain etched for only 14 s past t_i [Fig. 3(g)] indicates that pores with ~100 nm diam have already formed. It is important to point out that these samples with different morphologies produce rather similar PL spectra, with only slight differences in the wavelength of peak emission.

We have used the doping dependence on t_i to obtain *selective area photoemission* in PoSi. Localized Ga^+ FIB implantation and masked B^+ broad beam ion implantation into n-type Si followed by rapid thermal annealing (RTA) resulted in selective PoSi formation in the implanted regions during stain etching. An example using Ga^+ FIB implantation into n-si is shown in Fig. 4. The larger square, with dimensions of 540×540 μm^2, was implanted into ~0.1 Ω cm n-Si at 10 kV with a dose of $10^{15}/cm^2$ and then annealed at 550 °C for 60 s. This sample was then stain etched for a total time of t_i plus 1 min. A second sample consisting of 3.5 and 0.5 μm lines was implanted into 3 Ω cm n-Si at 30 kV with 10^{14} Ga^+/cm^2 and annealed at 600 °C for 30 s. This sample was also stain etched for a total time of t_i plus 1 min. Upon UV excitation, photoemission from the implanted regions only was clearly observable. As shown in Fig. 4, the pattern with 0.5 μm lines is quite sharp, indicating that submicrometer resolution is achievable with this process. This represents a considerably higher resolution than for the image projection lithography process previously reported[9] for anodized porous Si. The dark background surrounding each pattern is unimplanted n-Si. During visual observation, the colors are the same for both samples: orange-yellow in the implanted regions and dark blue background. Ga^+ and B^+ implanted samples exhibited visually similar color luminescence in the implanted regions. For samples processed without RTA, the implanted region had a much longer t_i than the surrounding area, leading to a PL image complementary to the implantation pattern. The PL spectrum obtained from the large Ga^+-implanted square is quite similar to those obtained from stain-etched unimplanted substrates, with a peak at 626 nm (see Fig. 2). The surface of the 10 kV

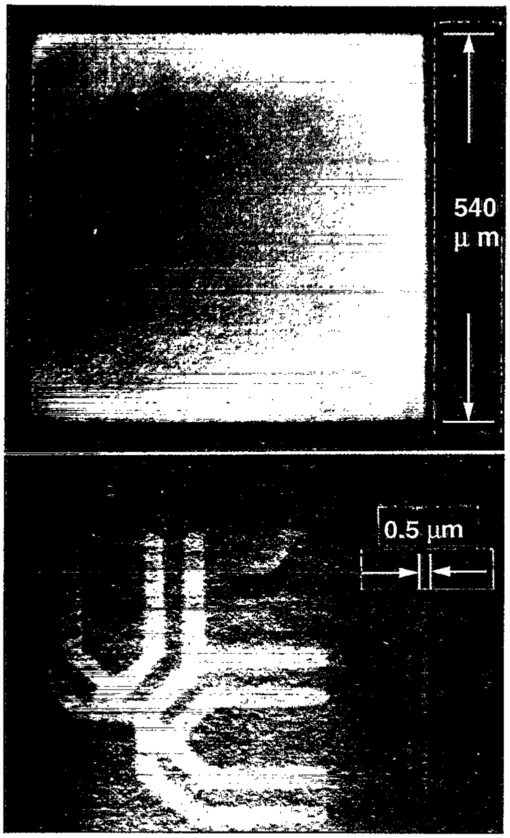

FIG. 4. FIB Ga$^+$ implantation-induced localized photoemission patterns. Large square implanted at 10 kV with $10^{15}/\text{cm}^2$. Line pattern with 3.5 and 0.5 μm linewidths implanted at 30 kV with $10^{14}/\text{cm}^2$.

Ga$^+$FIB-implanted sample [Fig. 3(h)] is considerably smoother than that of stain-etched unimplanted samples. Only occasional pores, with dimensions $\leqslant 100$ nm, are observed at higher magnification.

In summary, a significant doping dependence of the incubation time for PoSi formation has been observed. In conjunction with FIB implantation, this effect has been utilized to produce selective-area photoemission in PoSi with submicrometer resolution for the first time. This process can be easily incorporated into conventional semiconductor fabrication technology. This work was supported in part by SDIO/IST and monitored by ARO, under Grant No. DAAL03-92-0290. The authors are pleased to acknowledge the encouragement of L. Lome, R. Trew, and J. Zavada and the assistance of P. Chen with the FIB implantation and of W. Bresser with the PL measurements.

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