Photoluminescence of Porous Silicon

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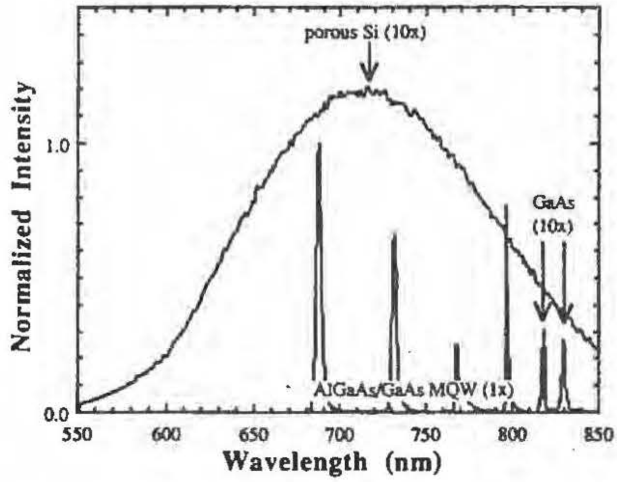
Porous silicon was discovered by Uhlir in 1956 [1] while electrochemically etching silicon in HF to remove defects created by mechanical shaping, but its photoluminescence was not reported until 1984 [2]. Prior to this time, silicon was thought to be an optically "dead" material due to its indirect and relatively small band gap of 1.1 eV [3]. The recent explosion of interest in porous silicon followed Canham's assertion that the photoluminescent properties could be attributed to quantum confinement [4]. Photoluminescence from porous silicon layers (PSL) is comparable in intensity to that of direct gap compound semiconductors like GaAsP [5], but PSLs have the added advantage of being easy and inexpensive to produce as well as being more readily integrated into standard silicon circuits [6].



A wide range of HF concentrations and current densities are employed in the preparation of PSL [1, 2, 4, 5, 7]. A proposed mechanism of silicon dissolution to create "quantum wires" involves nucleophilic attack of F- on Si-H bonds, producing H_2 and SiF_6^{2-} while depleting the holes of p-type Si [8]. Increased etch time results in increased photoluminescence intensity as well as a blue shift of the emission band peak [4, 9]. Thermal studies of PSL [9] show a decrease in photoluminescence above 300°C that can be regenerated with a brief HF etch. Once the PSL are heated above 450°C, the photoluminescence cannot be restored. PSL have also been shown to react with water to form Si-H and Si-O-Si [10] on their surfaces.

Several sources for the photoluminescence of PSL have been proposed, including siloxene ($Si_6O_3H_6$), amorphous silicon and quantum confinement [11]. Other theories include surface contaminants [12, 13], silicon hydrides [9, 14], and phonon-aided emission [15]. Siloxene has been known since 1922 and has photoluminescence that can be "tuned" via chemical substitution or annealing in air [16]. The photoluminescence and reactivity of PSL and siloxene are similar [17]. XPS studies of porous Si show, however, that carbon and oxygen are only trace impurities and the surface of PSL are not highly ordered [2, 12]. This is considered to be evidence for the presence of amorphous Si, which is known to have photoluminescence at 730 nm.

The primary evidence for quantum confinement is the inverse correlation of the peak emission energy with feature size [4, 8, 18, 19]. This theory is additionally supported by the observation that photoluminescence from Si nanocrystallites varies with the particle size [20]. Lifetime studies also show dependence on size, decreasing as confinement causes electrons and holes to recombine at an accelerated rate [21].

Several applications are envisioned for PSL [22]. Because the etching is enhanced by light, intensity of illumination can be varied and the surface mapped into a diffraction grating [23]. This also has potential for optical data storage. PSLs are candidate materials for optical computers. The observation of reversible quenching of PSL luminescence by solvents might indicate a future for PSL chemical sensors [24]. Further extending the scope of these materials, PSLs on sapphire are being investigated for integrated circuits and flat-panel displays [25].

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