

Electro- and photoluminescence in thin films of porous silicon

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A reddish-orange electroluminescence has been observed from layers of porous silicon produced by anodic etching of crystalline plates of *n*- and *p*-type Si. This luminescence arises on the positive branch of the current-voltage characteristic. Its intensity increases in proportion to the current through the sample. Photoluminescence spectra of the same layers were recorded. The structure and composition of the luminescent layers were studied by electron, x-ray, photoelectron, and Auger spectroscopy. The layers of porous silicon are an inhomogeneous system consisting of crystalline Si near the substrate, which converts into an oxide with fragments of unoxidized Si near the surface.

Interest in the visible luminescence of porous silicon first arose in 1990 (Ref. 1) and has increased continuously since then. The reason for the interest is the fundamental problem of the change in the band structure in the quantum wires of porous silicon and the conversion of this material into a direct-gap material.^{2,3} These effects are, moreover, of much practical importance, in connection with the development of silicon sources of visible light. Such sources are required, in particular, for organizing optical links in very-large-scale integrated circuits. They are potentially of interest for the development of optical data processing systems based on silicon integrated-circuit technology.

From the practical standpoint, the most important topic is the electroluminescence, which makes possible the development of an emitting device which can be excited and controlled by an electrical signal. An electroluminescence in the visible range has been observed in structures containing porous silicon in several studies. The transparent upper electrode has been made of Au, ITO (Refs. 4 and 5), and *n*-type SiC microcrystal films.⁶ An electroluminescence has also been observed⁷ during anodic oxidation of porous silicon in aqueous solutions of HCl and KNO₃. In all cases, the luminescence intensifies with increasing current through the structure, although it remains low.

At this point, it is difficult to understand the mechanisms for the electro- and photoluminescence of porous silicon because of gaps in our knowledge about the structure of this material. This is an extremely complex entity and can furthermore be produced in various modifications.⁸ Our purposes in the present study were to observe the electro- and photoluminescence of porous silicon and to study the structure of films which were grown.

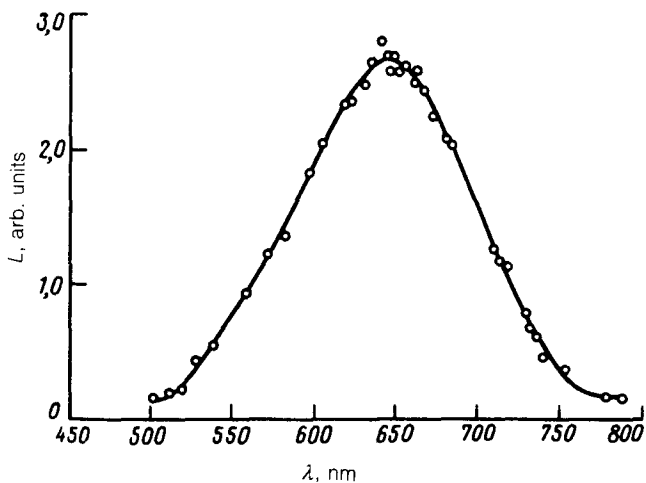


FIG. 1. Photoluminescence spectrum of porous silicon. L —Luminescence intensity; λ —wavelength.

The test samples were grown by electrolytic anodizing with a 1:1 solution of HF and isopropyl alcohol at a current density of 5–10 mA/cm² through the electrolytic cell. The n - and p -type Si plates had carrier densities ranging from 2×10^{19} to 1×10^{14} cm⁻³. The thicknesses of the porous silicon films were 1–10 μ m. A semitransparent gold contact (with a 50% transmission), with an area of 0.36 mm², was deposited on the porous silicon for the electroluminescence measurements.

The photoluminescence in the thin films was observed with the help of a Specord M400 spectrophotometer as the test structures were illuminated with a Cd-vapor laser ($\lambda = 0.44 \mu$ m). Figure 1 shows a photoluminescence spectrum. The intensity peak ranges from 0.64 to 0.68 μ m, depending on the particular deposition conditions. Some of the samples exhibit an intensity decrease in the course of cyclic measurements, without any change in the energy position of the peak. The photoluminescence is observed for samples on all types of substrates used. When the sample is immersed in HF, the photoluminescence intensity of the samples initially increases and then decreases; the intensity peak shifts to a longer wavelength, depending on the time the sample is left in the acid.

The electroluminescence, uniform over the surface area of the sample, was observed in p -Si-(porous silicon)-Au sandwich structures when a negative bias voltage was applied to the metal upper electrode. The current-voltage characteristic is of a rectifying nature. A reddish-orange electroluminescence is observed visually at electric fields above 10^4 V/cm. Figure 2 shows the integrated electroluminescence intensity versus the current through the sample. The behavior is quadratic. Most of the samples exhibit an electroluminescence which remains stable over time. In several samples, however, the electroluminescence takes the form of a brief flash over the entire surface area of the sample, accompanied by an abrupt decrease in the current through the sample.

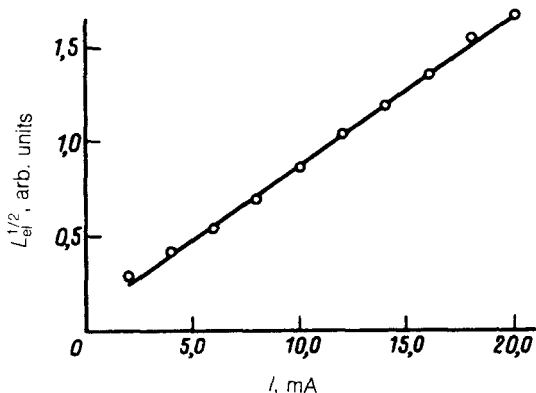


FIG. 2. Electroluminescence intensity L_{el} versus the current through the sample, I .

Samples made from the same plate used to prepare the samples for the electroluminescence measurements were studied by scanning electron microscopy (with a JEOL JSM-840 microscope, made by a Japanese company), by x-ray emission spectroscopy with electron-beam excitation (with a JEOL JXA-5A microanalyzer), and by photoelectron and Auger spectroscopy with x-ray excitation (Mg $K\alpha$ radiation, XSAM-800 ultrahigh-vacuum electron spectrometer, made by a British company). The test samples in the electron microscope and the microanalyzer were in a vacuum ($\sim 10^{-5}$ Torr) much lower than that in the electron spectrometer ($\sim 10^{-9}$ Torr), and the pressure of hydrocarbons was much higher. These factors had a decisive effect on the duration of the visually observable cathodoluminescence. In the low vacuum, radiation doses less than 10^{-2} C/cm² (the absorbed current) essentially quenched the luminescence, while quenching did not occur in the high vacuum at doses up to 3×10^{-2} C/cm².

Examination of the surfaces of the samples by electron microscopy and by visual cathodoluminescence revealed that the orange luminescence is excited in a nonuniform fashion along the surface. Cathodoluminescence was not observed on a transverse section of a sample. The thickness of the layer of porous silicon which formed during the electrochemical treatment was ~ 2 μ m.

Electron spectroscopy of the surfaces (the analysis depth was ~ 40 Å) revealed atoms of only Si, O, and C (hydrocarbon fragments), with a few F atoms. The great majority of the Si atoms in this layer are in a state of complete oxidation, although there are some ($\sim 10\%$) unoxidized Si atoms.

Examination of the samples by x-ray spectroscopy (Si $K\beta$ radiation) at various penetration depths (from 3000 Å to 5 μ m) of the exciting electrons (with energies varied from 25 to 5 keV) revealed that at the top the film of modified silicon consists primarily of an oxide layer ~ 2500 – 3000 Å thick) containing unoxidized silicon (Fig. 3). Over depth, this oxide converts into a layer of unoxidized silicon.

In summary, this study has shown that the samples of porous silicon which we prepared constitute an inhomogeneous system. The material near the substrate is crystalline porous silicon; near the surface the material becomes an oxide layer with fragments of unoxidized silicon.

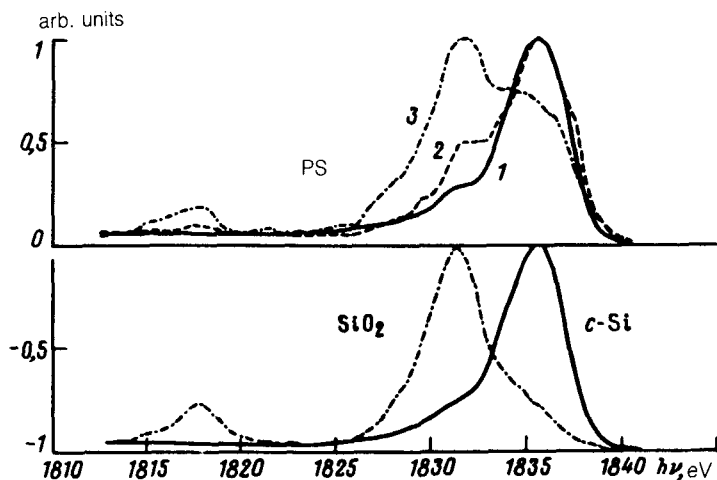


FIG. 3. Si $K\beta$ x-ray emission spectra of samples of porous silicon (PS) and fused quartz (SiO_2). Spectra 1, 2, and 3 were recorded at various penetration depths of the exciting electrons (5, 1, and $0.3 \mu\text{m}$) and at various electron energies in the primary beam (25, 8, and 5 keV, respectively).

The nature of the changes which occur in the photoluminescence when the upper layer is etched off in HF indicates that the upper layers of porous silicon play an important role in the onset of luminescence. Regions with a composite structure (fragments of Si in a SiO_2 matrix) may be the most effective in the luminescence. The quadratic current dependence of the electroluminescence indicates that the radiative recombination in such regions is bimolecular under double-injection conditions.

Constructing a suitable physical model for the luminescence in porous silicon will require determining the nature of the emitting regions and a detailed study of the electronic aspects of the process.

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