Pulsed anodic etching: An effective method of preparing light-emitting porous silicon

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A pulsed anodic etching method is developed to prepare light-emitting porous silicon. Under the same equivalent etching condition, pulsed etching can yield a more uniform porous silicon film with stronger photoluminescence intensity than the film prepared by ordinary dc etching. The atomic force microscopic observation shows that the porous silicon surface prepared by pulsed etching contains more widely separated Si columns but with steeper sidewalls, which are believed to result in the improvement of quantum confinement. The thickness of pulse etched porous silicon film is found to be much larger than that of a dc etched sample. © *1996 American Institute of Physics.* [S0003-6951(96)00417-X]

To fabricate light-emitting porous silicon (PS), the most commonly used method is anodic etching of a Si wafer in HF solution.[1] A self-adjusted mechanism makes the anodic dissolution of Si occur basically at the pore tips.[2–4] In the dc anodic etching process, the chemical reaction of HF with Si will lead to the reduction of HF concentration inside the pore and thus slow down the etching process itself. Moreover, the species produced in the etching process will form bubbles on the wall surfaces of pores. This in turn prevents the progress of the etching process. We follow the brief suggestion of Bomchil *et al.*[5] that it may be better to carry out the anodic etching process not in a continuous way but rather in an intermittent mode. It is expected that during the period of pause of anodic current, the desorption of the bubbles and the interchange of HF species between the inside and outside of the pores will occur, which may possibly keep the anodic etching process in a better condition than that of dc anodic etching. If it is true, the periodic suspension of the anodic current would benefit the process of PS formation. In this work, a pulsed anodic etching method is developed to prepare light-emitting porous silicon. The advantages of this technique over the ordinary dc anodic etching are demonstrated.

A pulsed power supply with the output voltage and duty cycle adjusted by a micro computer was used to feed the current through the anodic etching circuit, i.e., the series of the etching bath, and a standard resistance of 1 Ω. The wave forms of voltage and current were monitored during the etching process. As seen from Fig. 1, in the dc anodic etching process, the current decays with the etching time and reaches a stabilized value after a time period of about 20 ms. This reflects the dilution of the HF concentration inside the pores. For the pulsed anodic etching, the process can be carried out in two different modes: the constant voltage amplitude mode and the constant current amplitude mode. Figure 2 shows the wave forms of voltage and current in the constant voltage mode operation. The amplitude of the anodic current is larger than the stabilized current in Fig. 1, which implies that the partial recovery of HF concentration inside the pores is achieved.

The PS samples were prepared on p-type Si(100) wafers with the resistivity of 1–1.5 Ω cm. The solution of 49% HF: ethanol=1:1 was used as the etching solvent. It was found that for the PS samples prepared by pulsed etching the achievement of luminescence is easier as compared with samples prepared by dc anodic etching. Also, the surfaces of the former are more uniform and flat. The pulsed etching usually yields PS samples with shiny mirrorlike surfaces. Figure 3 shows the photoluminescence (PL) spectra measured under the excitation of the 441.6 nm line of a He–Cd ion laser. The sample a and c were prepared by dc anodic etching with the current density of 2 and 10 mA/cm^2, etching time of 5 min, respectively. The samples b and d were etched by pulsed current at the peak current density of 2 and 10 mA/cm^2, with repetition rates of 100 and 2000 Hz, duty cycles of 0.05 and 0.2, etching times of 100 and 25 min, respectively. Under the equivalent etching condition, i.e., the same current density times effective etching time, 10 mA/cm^2×min for samples a and b, 50 mA/cm^2×min for c and d, the enhancement in PL intensity by pulsed anodic etching is obvious from Fig. 3. By using the cross sectional scanning electron microscope, the thicknesses of samples a, b, c, and d

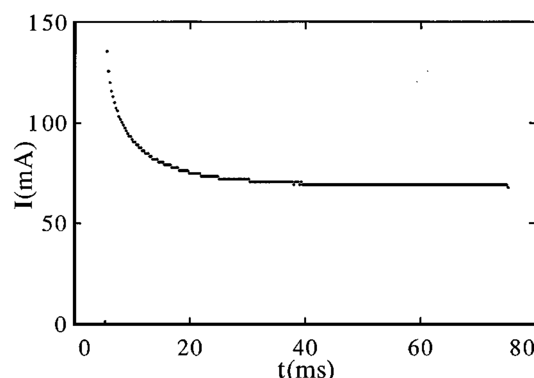

FIG. 1. The anodic current decays with the etching time at a constant voltage of 0.4 V.

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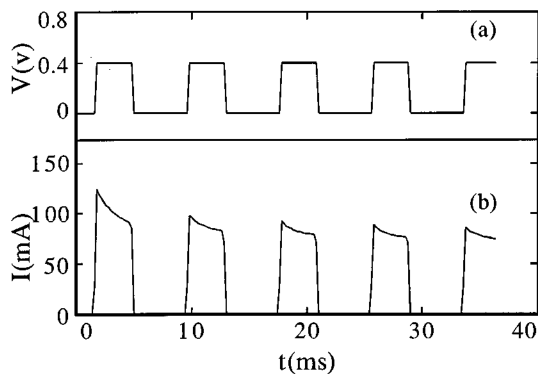

FIG. 2. The wave forms of (a) voltage and (b) current in the constant voltage mode of a pulsed etching process.

are 0.6, 2.4, 4.8, and 6.6 μm, respectively. The thickness difference between the dc etched samples and the samples prepared by pulsed etching becomes smaller with increasing current density and duty cycle. The thickness of sample b is four times that of sample a, while the thickness of sample d is only 50% larger than that of sample c. In Fig. 3, it is clearly shown that the PL enhancement of sample group of c

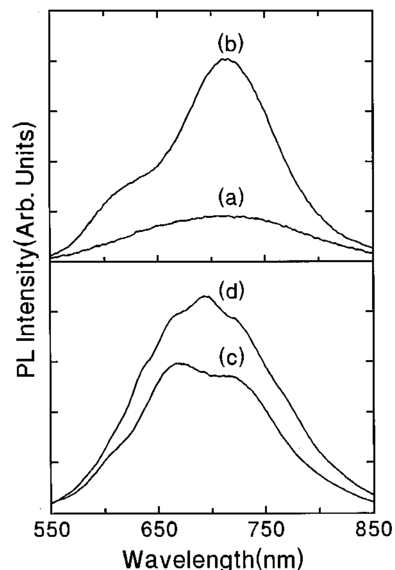

FIG. 3. The photoluminescence spectra of porous silicon samples prepared at current density of 2 mA/cm^2 by (a) dc anodic etching for 5 min, (b) pulsed anodic etching with duty cycle of 0.05 and repetition rate of 100 Hz for 100 min, and at current density of 10 mA/cm^2 by (c) dc anodic etching for 5 min, (d) pulsed anodic etching with duty cycle of 0.2 and repetition rate of 2000 Hz for 25 min.

FIG. 4. AFM images of porous silicon samples: (a) dc etching at 2 mA/cm^2 for 5 min, (b) pulsed etching at 2 mA/cm^2 for 100 min with the duty cycle of 0.05 and repetition rate of 100 Hz, (c) dc etching at 10 mA/cm^2 for 5 min, (d) pulsed etching at 10 mA/cm^2 for 25 min with the duty cycle of 0.2 and repetition rate of 2000 Hz.

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and d is smaller than that of sample group of a and b. The above results verify that the pulsed anodic etching will create a thicker PS layer than the dc etching under the same integrated etching time, especially for samples created by pulsed etching with a smaller duty cycle and lower current density.

The surface morphologies of PS samples were observed by a Digital Instruments Nasoscope III atomic force microscope (AFM). During the tip scanning the ''tapping'' mode was adopted to prevent the damage of the sample surface or the tip. Very stable AFM images could be obtained for most of the PS samples. The radius of curvature of the tip was about 10 nm giving rise to a lateral spatial resolution of about 2 nm on a flat surface. The scan range was larger than 300 nm. Figure 4 shows the AFM images of two dc etched PS samples (a) and (c) and two pulsed etched PS samples (b) and (d). The features here seem to be comparable with or even better in some regards than those previously reported.[6–9] The most obvious difference between the dc etched and pulse etched PS samples with same integrated etching times is the steepness of the Si columns. The surfaces of pulse etched samples (b) and (d) contain somewhat more widely separated Si columns but with steeper sidewalls than the dc etched samples (a) and (c). The etching depth of sample (b) is even larger than that of sample (c). The former was etched under the equivalent current density-time product of 10 mA/cm$^2\times$min, while the latter was etched with larger current density-time product of 50 mA/cm$^2\times$min. The dimensions of the Si pillars could be estimated from the AFM images. For smaller Si pillars, the sizes of their top parts are figured to be 5–8 nm. Since the broadening effect is inevitable, especially for the surfaces with larger fluctuation structures, the pillar sizes above are overestimated. After a simple correction to subtract the broadening effect by the finite size of the tip, the size of pillar top is estimated to be no larger than 3 nm, which is small enough to cause the quantum confinement effect. By contrast, in the work reported previously, the structures of the dimensions necessary for quantum confinement were not detected.[9]

With observation by the naked eye, the porous Si film prepared by pulsed etching shines a uniform interference color in the sample area of 3 cm^2, while the interference color varies from the center to the edge of the dc etched sample. This indicates that pulsed etching usually yields PS layer with a uniform thickness, in spite of more roughness under the atomic force microscopic observation.

In summary, we have found that the pulsed etching is a more effective way than the dc etching method to prepare light-emitting porous silicon. The periodical intermittence of the anodic current apparently causes the recovery of HF concentration inside the pores and could optimize the etching conditions. Thicker and more uniform porous silicon layers with higher photoluminescence intensity are easy to prepare. Atomic force microscopic observations of the surface reveal that the pulsed etching creates isolated Si pillars with steeper sidewalls, which are in favor of achieving quantum confinement effect.

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