APPLIED ORGANOMETALLIC CHEMISTRY, VOL. 12, 337–340 (1998)

Structured Luminescent Silicon Produced with Laser-assisted Etching

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We present an investigation into a new technique for producing luminescent porous silicon with controlled lateral microstructure. The process is based on the effect of laser-assisted stain etching of silicon with hydrofluoric acid solution. With the further goal of preparing two-dimensional periodical arrays of luminescent microdots, we studied the accuracy of the technique by etching single submillimetre structures with a low-power laser. The size and exact position of the etched area are controlled by laser focusing and movement, respectively, with submillimetre accuracy. Samples exhibit orange luminescence when illuminated with UV or blue light.

We have studied the dependence of the efficiency of the luminescence, the structure and the rate of etching on parameters such as the HF concentration, the intensity and wavelength of illumination and the doping level of the silicon wafer. Optimization of the process parameters, and consistency with assumed mechanisms of luminescence and etching process, are discussed. © **1998 John Wiley & Sons, Ltd.**

Appl. Organometal. Chem. **12**, 337–340 (1998)

Keywords: porous silicon; luminescence; light-assisted etching; atomic force microscopy

Received 20 November 1997; accepted 6 February 1998

INTRODUCTION

Silicon has predominated over other semiconductors in microelectronics for a long time, and is likely to do so in the future. However, it is an extremely inefficient light emitter. It is important to develop the technology that would allow optical and electronic devices to be integrated on silicon wafers. After the discovery of efficient visible photoluminescence (PL) and electroluminescence (EL) from porous silicon (PS) in 1990,[1] a great amount of research on PS preparation and properties was stimulated all over the world.

Etching in hydrofluoric acid (HF) is used to produce porosity in silicon. Crystalline silicon is not usually etched with HF alone. It was found that when holes are driven to the water–solution interface by an electric current, etching is stimulated. The process is called anodization, as the silicon wafer acts as a positive electrode. Much experience has been accumulated on preparation of luminescent PS by this technique.[2] The generally accepted mechanism of anodization is shown in Fig. 1. The process of detachment of one Si atom can be expressed by Eqns [1] and [2].

$$Si_nH_2 + 4F^- + 2H^+ + 2\oplus \longrightarrow Si_{n-1}H_2 + SiF_4 + H_2 \quad [1]$$

$$SiF_4 + 2HF \longrightarrow SiF_6^{2-} + 2H^+ \quad [2]$$

When an electric current through the wafer is used to supply holes, it is impossible to define areas of preferential etching. Conventional masks cannot be used, as no masking material is resistant to HF.[3] Fortunately, another way of supplying holes to the interface has been proposed.[4] Laser illumination was used to generate carriers in bulk silicon. For n-type samples, the Schottky barrier[5] at the interface helps to bring holes to the surface. Using this mechanism we can produce the desired lateral structure of the porous layer by structuring the illumination pattern. This will give us a fast method of preparing two-dimensional (2D) arrays of luminescent dots. Provided the technical problem of individual addressing is solved, this may be of use for microscale digital displays, multicore fibre optics, silicon-based optical data storage etc. Examples of possible structures of illumination patterns are shown in Fig. 2. The capability of the technique was demonstrated recently.[6] The production of diffraction gratings of different spacing by etching in silicon was described, the periodic structure being induced by interference of two laser beams. However, the energy measured in diffrac-

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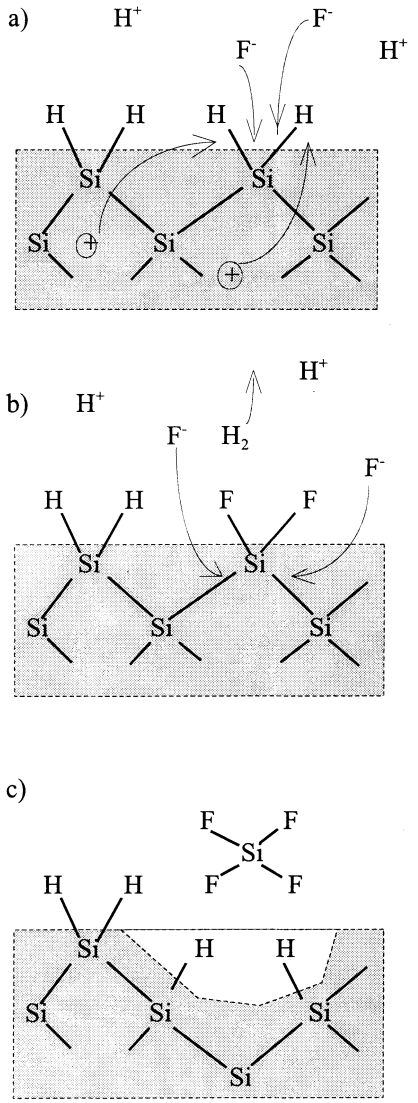

Figure 1 Etching mechanism. Initial surface is passivated with hydrogen; (a) holes coming from the bulk attack Si–H bonds and enable fluorine ions to substitute for hydrogen; (b) Si–Si bonds near the attacked atom are weak and easily broken by other fluorine ions; (c) a Si atom is finally detached in the form of SiF_4.

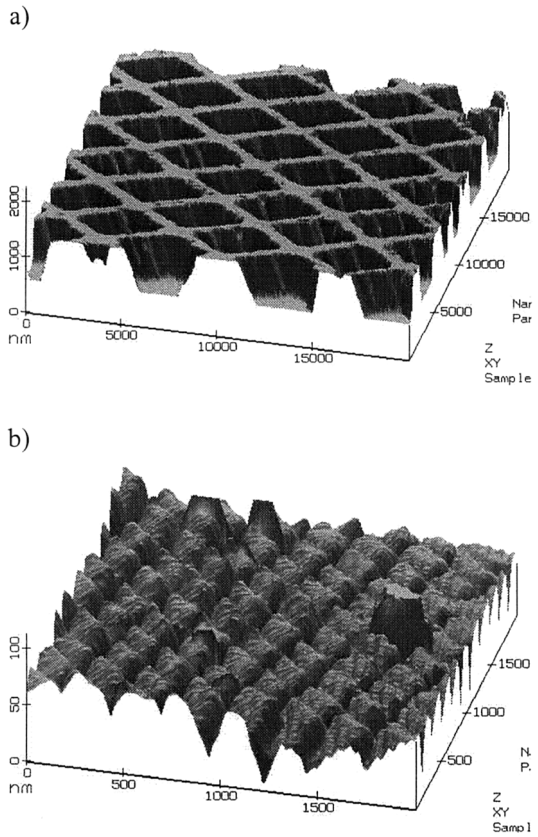

Figure 2 Examples of illumination patterns recorded on a negative photoresist: (a) projection of the 100 μm copper grid with 20× reduction (the total image is 20 μm × 20 μm ; (b) interference pattern of four laser waves of in-plane polarization. The whole image is 2 μm × 2 μm; the wavelength used (λ) was 442 nm. With the grazing angle of incidence, features nearly as small as $\lambda/2$ can be produced.

tion orders is low. Low contrast of the etched pattern could be caused by carrier diffusion or by low contrast of the illumination itself. Optical materials are not resistant to HF, which is why it is difficult to bring light to the sample without distortion of the image or interference pattern. To study methods for improving the precision of the technique was the aim of our research.

EXPERIMENTAL

n-type (111) silicon wafers were used, with 10 Ω cm resistivity. Less resistant wafers are more easily etched, but the resulting surface is rougher with less fine structure. In any case, highly doped material is of less interest for electronic applications. p-type silicon showed no light-assisted etching. Samples were washed in ethanol and placed on the bottom of a polythene cell containing 40 wt% HF/ethanol solution (2:1). He–Ne laser light was used for illumination. A 1 mW laser beam was focused through the top window and was adjustable by micropositioners to control the diameter and the position of the illuminated area.

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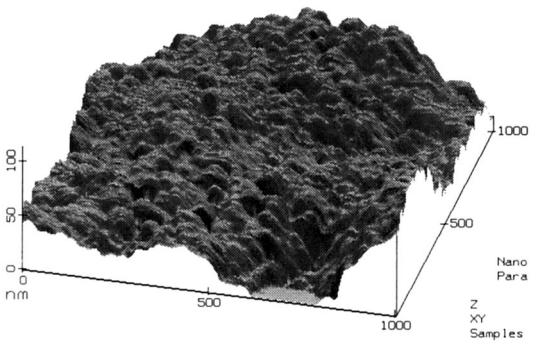

Figure 3 A typical surface of the treated silicon wafer sample. The image size is 1 μm × 1 μm. The AFM tip cannot penetrate into the deep pores to show the actual structure.

parameters, such as wafer doping, HF concentration, laser wavelength and power density, were investigated. Surface roughness of the etched areas was studied using a Nanoscope-II atomic force microscope (AFM), and PL spectra were measured on a scanning spectrograph with a multialkali air-cooled detector, using excitation from a Kimmon He–Cd laser.

RESULTS AND DISCUSSION

A typical AFM image of the PS produced is shown in Fig. 3. The resulting porous layer is mesoporous, with fine structure (<50 nm) superimposed on the submicron roughness of the surface. The AFM tip has a blunt angle shape, which is why the image does not show the depth of the pores or any smaller structures inside. The smallest features on our images appear to be about 50 nm in size, which could correspond to features of less than 20 nm, if one takes into consideration the shape of the end of the AFM tungsten tip. To explain the visible luminescence of PS, quantum confinement models require a feature size on a scale of less then 10 nm (usually 2–3 nm sizes are quoted)[7,8,] which cannot be seen on our images.

We have made the following observations.

(1) The illumination power seems to be of crucial importance. The depth of the structure increases with the power density (as controlled by beam focusing), whereas the size of the visible features is the same (Fig. 4). With less then 0.1 mW mm^{-2} (first image) there is no etching at all. For more then 10 mW mm^{-2} the resulting image saturates, and no further reduction of feature size is detected. When etched samples are left in a solution without light, the porous layer dissolves slowly, over a period of 10–20 min. The surface remains rough, but luminescence is not present. This means either that there are enough carriers between the pores to destroy the structure, or that holes are not needed to etch the affected layer. On the other hand, when illumination is present, the light penetrates through the porous layer and is absorbed in the bulk, and this supplies holes to the ends of the pores and stimulates pore growth. For this process to compete successfully with the dissolution of the porous layer, the power density has to exceed a certain limit described above.

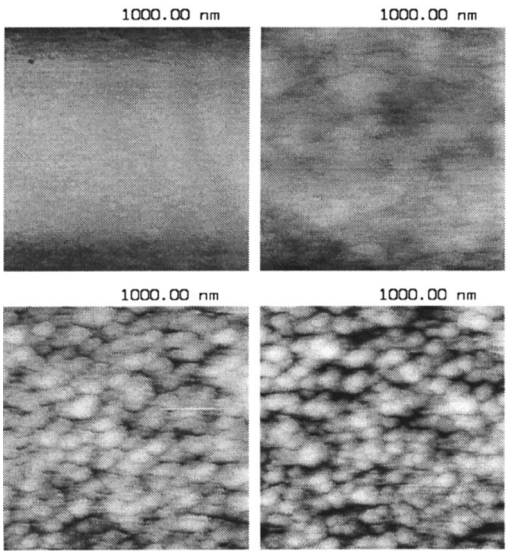

Figure 4 Surface roughness for four monotonically increased illumination densities: from 0.1 mW mm^{-2} (top left) to 10 mW mm^{-2} (bottom right).

(2) Initiation of the etching of a fresh surface takes a very different time from sample to sample (from several seconds to several minutes). This shows the importance of the surface condition. Once etching has started, the porous layer growth rate damps with its thickness, the brightness of the sample obtained saturating within 10 min. We explain this by the same competition of pore growth with dissolution of the top layer.

(3) When blue (488 nm) or green (514 nm) light was used, the luminescence of the resulting porous layer was much weaker. This result was previously explained by the assumption that the

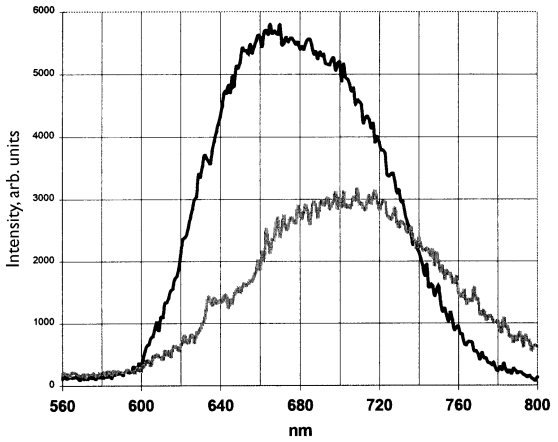

Figure 5 PL data for two different excitation wavelengths: 325 nm (black trace) and 442 nm (grey).

bandgap of PS is modified in such a way that it becomes transparent to red light but absorbs blue, so that red light stimulates pore growth whereas shorter wavelengths dissolve the porous layer.[4] However according to the quantum confinement idea, etching with blue light would produce a further decrease in feature size, the bandgap would increase more and the porous structure would become transparent to the blue light as well. We would end up with finer structure, which does not occur. On the other hand, experiments with anodization of n-type silicon show that UV or blue illumination during etching improves nanoscale porosity.[2] We think that the difference in extinction coefficients is important (0.02 for a 630 nm wavelength compare to 0.17 for 440 nm): the mean absorption depth is one order less for blue light, and this generates carriers in the porous layer, causing it to dissolve.

(4) Samples with less resistivity (more doping) are etched better, but give just a rough surface rather than a nanoporous layer. Excessive concentration of free electrons (majority carriers) makes it difficult for the holes to play their role in the assumed etching mechanism. Besides, with a thinner Schottky barrier, holes are driven to the surface less efficiently.

(5) Ethanol content does not seem to have much influence on the process. In contrast to anodization, where the presence of ethanol is essential to let the etchant into deep pores, in our experiment it only slows down the process because of a decrease in HF concentration. This suggests that very deep pores are not formed.

(6) Samples have visible orange PL, and the spectra for UV (325 nm) and blue (442 nm) excitations are shown in Fig. 5. The PL has a wide Gaussian shape, which is usually explained by the size distribution of quantum-size features. The curves obtained for different excitation wavelengths are shifted 40 nm from each other. Although both curves are centred in the red region, the visible light seems to be orange, possibly because of the increased sensitivity of eyes to blue–green luminescence of silicon oxide film, which is always present. The laser power was five times greater for excitation at 442 nm than at 325 nm, which perhaps is why the right-hand wing of the 442 nm (grey) curve is not within the envelope of the 325 nm (black) curve. All other conditions were the same for both spectra.

CONCLUSIONS

Submillimetre areas of luminescent porous silicon were produced by light-assisted stain etching. With adequate advances in technology, the technique might be of great importance for integration of optical devices in silicon-based microelectronics. The effect of different parameters on the process was studied. Our observations improve the understanding of the stain etching of silicon. Some results would also be of interest for theoretical physics, helping to clear up issues such as the mechanism of luminescence of porous silicon.

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