Microstructural investigations of light-emitting porous Si layers

I. George, M. S. Anderson, W. T. Pike, T. L. Lin, and R. W. Fathauer
Center for Space Microelectronics Technology, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California 91109

K. H. Jung and D. L. Kwong
Microelectronics Research Center, Department of Electrical and Computer Engineering,
The University of Texas at Austin, Austin, Texas 78712

(Received 22 November 1991; accepted for publication 27 January 1992)

The structural and morphological characteristics of visible-light-emitting porous Si layers produced by anodic and stain etching of single-crystal Si substrates are compared using transmission electron microscopy and atomic force microscopy (AFM). AFM of conventionally anodized, laterally anodized and stain-etched Si layers show that the layers have a fractal-type surface morphology. The anodized layers are rougher than the stain-etched films. At higher magnification 10 nm sized hillocks are visible on the surface. Transmission electron diffraction patterns indicate an amorphous structure with no evidence for the presence of crystalline Si in the near-surface regions of the porous Si layers.

The discovery of visible light emission in anodically etched porous Si films has generated considerable interest in determining the nature of the light emission and the relationship to the microstructure of the porous material. It has been suggested that quantum confinement effects due to the formation of small crystallites of Si in the porous layer are responsible for the visible light emission. Indeed, transmission electron microscopy (TEM) images of narrow Si columns believed to be the light emitting structures have been presented. Recently, visible luminescence peaked in the red was observed from stain-etched Si wafers of different dopant types, concentrations and orientations produced in solutions of HF:HN03:H20. Stain films on Si wafers have been studied for over 30 years, and have been suggested to be similar in nature to the anodically produced porous Si films. In this letter the microstructure of light-emitting layers on two types of anodically etched Si and on stain-etched Si are compared using atomic force microscopy (AFM) to study the surface morphology and transmission electron microscopy (TEM) to examine their crystallinity.

Anodically etched films were produced using two types of anodization processes: a lateral anodization process described in detail elsewhere, and by a conventional anodization process. In the lateral anodization process, the Si wafer is clamped in a vertical position, only partly immersed in the anodization solution, so that the current travels laterally along the wafer. P-type (100) Si wafers with resistivities of 2-10 Ω cm were anodized in a 1:1 dilution of commercially available 49% HF in deionized water. Most of the stain films were produced by immersion of Si substrates in solutions of HF:HN03:H20 with ratios of either 1:5:10 or 4:1:5 by volume. Reagents used were 49% HF, 70%-71% HNO3, and deionized water. By avoiding rapid evolution of gas during the etching process (typically 30 s to 10 min in duration) specular films were obtained.

Surface morphology observations were made in air at room temperature with a Digital Instruments (DI) Nanoscope IAFM. The AFM cantilevers had silicon nitride tips (half angle of 30°) on 100-μm-wide-legged cantilevers and tip radii estimated to be in the range of 5-20 nm. Several cantilevers were used for each type of substrate analyzed. TEM was performed on the samples using an ABT 002B 200 kV high-resolution electron microscope; TEM specimens were prepared by a cleavage technique to produce electron-transparent thin foils.

AFM images of the three types of films are shown in Fig. 1. The presence of columnar features is observed in the anodized films [Figs. 1(a) and 1(b)]; the stain-etched films were observed by AFM as having a smooth surface with pores dispersed within the layer [Fig. 1(c)]. A high-resolution AFM image of a laterally anodized sample is shown in Fig. 2(a). A line profile [Fig. 2(b)] at this resolution shows the presence of hillocks approximately 10 nm wide. As this width is comparable to the tip radius it should be taken as an upper limit of the true value. Similar hillock-type features are also seen in the conventionally anodized and stain-etched samples. Any pores present on the surface with sizes in the range of the tip dimensions would be imaged as having curved or flattened bottoms due to the limited tip penetration. The fractal nature of the porous Si surfaces is observed on comparing the AFM images obtained at various magnifications. This type of surface morphology could arise from layers having a wide range of pore sizes at the surface. The larger pores at the surface of the layers could result from the coalescence of several closely spaced smaller sized pores that have expanded laterally. Such wide distributions in pore sizes have been observed before using TEM.

It is apparent from the AFM results that there is no unique microstructure that can be correlated with light-emission. The surface morphology and structure of each porous Si layer depends on the preparation technique. The gross differences in morphology between the anodically etched films and the stain-etched films could be related to the nature of pore formation in the two types of layers: for the anodically etched films the external potential provides the driving force for Si dissolution producing uniformly
FIG. 1. AFM profile images of (a) a conventionally anodized sample, (b) a laterally anodized sample, and (c) a stain-etched sample.

rough morphology; in the stain-etched sample dispersed anodic and cathodic sites on the substrate are required to sustain the pore formation leading to localized pitting. The hillock protuberances observed in all the films with sizes in the range (<10 nm) required for quantum confinement could be the light-emitting features provided they were crystalline.

Cross-sectional TEM micrographs of thin-foil specimens were taken of anodically-etched and stain-etched samples. The laterally anodized Si film [Fig. 3(a)] consists of two distinct layers: a continuous uniform and finely textured lower layer and a fragmented coarse grained upper layer (low magnification AFM images of such films show a "dried lake-bed" morphology). Lateral anodization produces a nonuniform time dependant, distribution of electric current across the surface of the sample. An initially high current density abruptly falling during the etch would generate the observed microstructure. The stain-etched sample [Fig. 3(b)] contains a porous Si film of uniform thickness with a planar surface, although occasional dips in the film/Si interface are observed. Diffraction patterns obtained from both types of films showed them to be amorphous in nature. In order to confirm that the amorphous...
diffraction patterns were not the result of the thin-foil specimen preparation procedure, cross-sectional TEM was performed on wedge specimens prepared from the three types of films. Wedge specimens are prepared at room temperature by simple cleavage and therefore are not exposed to solvents, higher temperatures, or ion beams which are part of the thin-foil specimen preparation procedure. In all three instances, the diffraction patterns obtained from the light-emitting layers were amorphous in nature. A micrograph and diffraction pattern from the stain-etched sample is shown in Fig. 4.

Further confirmation of the amorphous nature of these films was obtained from reflection high-energy electron diffraction patterns taken from freshly prepared stain-etched samples introduced into a molecular beam epitaxy system. During the high-resolution AFM studies, no evidence of surface ordering was observed. Finally, x-ray photoelectron spectroscopy performed on both stain-etched and anodized films showed that the near-surface regions of the films were mainly composed of amorphous Si.

These results appear to contradict the conclusion reached by Cullis and Canham that quantum-size crystalline structures are responsible for visible light emission. A possible reason could be the specimen preparation technique used by these authors in which the specimens were prepared by scraping the porous Si layer off the surface. In this way it is not possible to determine the location of the Si crystallites in the porous Si layer. Our results are, however, consistent with previous results which report the formation of amorphous films when the porosity exceeds \( \approx 60\% \). Evidence that light emission occurs from amorphous rather than crystalline regions of porous Si films is discussed in depth elsewhere.

The formation mechanism of the amorphous film, whether by an electrochemical deposition process or by phase transformation, remains, as yet, unknown. In his work on stain-etched films, Archer suggests that the films consist of some form of silicon hydride that is formed during the etching process. Although we do not see evidence for the presence of a hydride film, a redeposition process could take place during etching whereby an amorphous film of hydrogen terminated Si is formed on the substrate surface. Alternatively, Veprek and co-workers suggest that in the limit of crystallite size of about 3 nm, the crystal lattice expansion of microcrystalline Si leads to an instability of the diamond structure with respect to the amorphous phase. Therefore it is possible that during the formation of porous Si from single crystal Si, small Si crystallites are produced that undergo spontaneous phase transformation when their individual sizes fall below the critical value of 3 nm.

In conclusion, light-emitting porous Si layers produced by anodization and stain-etching processes were compared. The surface morphology appears to be a function of the preparation technique. Very small (\( \approx 10 \) nm) features were observed on the surfaces of these layers. However, no evidence of crystallinity was obtained in the near-surface regions of any of the porous Si layers.

This work was performed by the Center for Space Microelectronics Technology and the Space Materials Science and Technology Section, Jet Propulsion Laboratory, California Institute of Technology and was supported by the Air Force Office of Scientific Research through an agreement with the National Aeronautics and Space Administration. Additional funding was provided by a JPL Director's Discretionary Fund.