Title
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Publication Date
1995-03-01

LBL-37086
UC-404

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Presented at the 9th International Conference on
Microscopy of Semiconducting Materials, Oxford, England,
March 20–23, 1995, and to be published in the Proceedings

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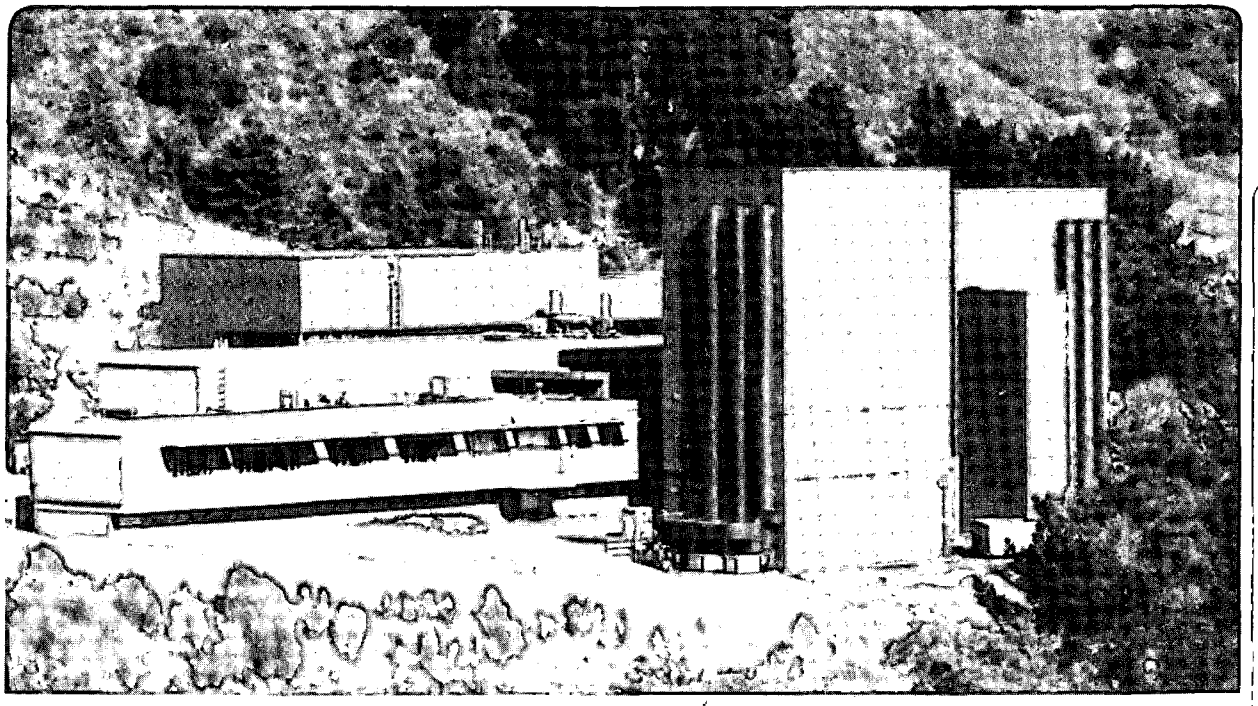

Prepared for the U.S. Department of Energy under Contract Number DE-AC03-76SF00098

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LBL-37086

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9th Int'l Conf. on Microscopy of Semiconducting Materials
Oxford, England
3/20-3/23/95

This work was supported in part by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Science Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098, and by the National Science Foundation under grant DMR-9202645.

Dynamic observation of electrochemical etching in silicon

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ABSTRACT: We have designed and constructed a TEM specimen holder in order to observe the process of pore formation in silicon. The holder incorporates electrical feedthroughs and a sealed reservoir for the electrolyte and accepts lithographically patterned silicon specimens. We describe the system and present preliminary, *ex situ* observations of the etching process.

1. INTRODUCTION

Porous semiconductors represent a relatively new class of materials formed by selective etching of a single or polycrystalline substrate. Although porous silicon has received considerable attention due to its novel optical properties (Canham 1990), porous layers can be formed in other semiconductors such as GaAs and GaP (Krumme and Straumanis 1967, Faktor et al. 1975, Chase and Holt 1972). These materials are characterised by very high surface area and electrical, optical and chemical properties that may differ considerably from bulk. The pore morphology can be controlled by adjusting the processing conditions and the dopant concentration. A number of novel structures can be fabricated using selective etching. For example, self-supporting membranes can be made by growing pores through a wafer (Searson 1991), films with modulated pore structure can be fabricated by varying the potential during growth (Munder et al. 1993), composite structures can be prepared by depositing a second phase into the pores and silicon-on-insulator can be formed by oxidising a buried porous layer (Tsao et al. 1989).

In all applications of porous silicon the ability to grow nanostructures controllably is critical. We are attempting to gain a better understanding of the formation mechanism of porous silicon by allowing pore formation to occur in real time within the microscope. We have designed and constructed a specimen holder for a JEOL 200CX TEM featuring a sealed reservoir which can be filled with the desired electrolyte (such as HF). Electrical feedthroughs are provided so that an anodization potential can be applied while in the microscope. The specimen itself requires a complex design to allow pore propagation laterally through an electron transparent region while avoiding the release of HF. We find that pores propagate at speeds of up to 100 nm s^{-1} on application of a 2-3V potential. Our aim in observing the dynamics of the process in real time (for example as a function of voltage) is to test different models of pore formation and to control the morphology of the pores produced. In this paper we will describe the issues we have encountered in setting up these experiments and present *ex situ* observations of pore formation. We ultimately hope to apply the experience gained to the study of different electrochemical processes and we will therefore discuss the extension of these techniques to other systems.

2. ANODIC ETCHING OF SILICON

Electrochemical etching of silicon is carried out by applying a potential of several volts between silicon and the HF electrolyte. Current densities of 1-100 mA cm^{-2} flow, silicon goes into solution as H_2SiF_6 and a network of unetched silicon is left behind. H_2 gas is a product of the reaction. The structures formed have been documented in considerable detail. In p-type silicon, the etching process leaves an interconnected network of filaments with typical dimensions 3-5 nm

(Cullis and Canham 1991, Smith and Collins 1992, Ross et al. 1995a). In n-type silicon, the pores can range in size from nanometers to microns and tend to grow in well defined crystallographic directions with a variable degree of branching (Theunissen 1972, Chuang et al. 1989, Smith and Collins 1992, Lehmann 1990, 1993, Searson et al. 1992).

The interfacial reactions which occur are reasonably well understood (see for example Smith and Collins 1992) and will not be discussed further here. However, knowledge of the overall electrochemical reaction does not give any information about the spatial distribution of the current during etching. It was in order to make a detailed study of models proposed to explain the morphology found in n-type silicon (Smith et al. 1988, Beale et al. 1985a, b, Erlebacher et al. 1994), including the formation of side branches and the reaction of the system to changes in the applied potential, that we decided to examine the pore formation process in real time.

3. DESIGN OF AN *IN SITU* ELECTROCHEMICAL SYSTEM

In order to observe electrochemical etching both the specimen holder and the specimen must be designed within fairly severe constraints. Etching must proceed in a well defined geometry within an electron transparent region while the specimen remains in electrical contact with the electrolyte, and this must all take place within the microscope vacuum. The specimen holder (figure 1) features an enclosed 3x4x6mm reservoir made of machinable ceramic in which the electrolyte is sealed. Electrical contact to the electrolyte is made by a platinum screw which extends into the reservoir and also acts as a means to fill the reservoir. The specimen is sealed into the other end of the reservoir using HF-resistant epoxy, leaving an area of about $1mm^2$ in contact with the electrolyte. The reservoir and specimen can be removed from the holder for testing.

The specimen itself requires a complex design to avoid the release of HF during etching (figure 2). The initial substrate was a lightly doped SIMOX wafer on which MBE was used to add a lightly doped barrier layer, a heavily doped "active" layer and a further barrier layer. This sequence was chosen to maximise the selectivity of the etching, since the order of reactivity for a given applied potential is $n^+ > p^+ > p^- > n^-$ (Smith and Collins 1992). The purpose of the buried oxide layer was twofold, firstly to act as a barrier to current flow within the bulk of the specimen and secondly to act as an etch stop for the $HF/HNO_3/HAc$ etchant which was used to form electron transparent windows by etching from the back surface. Before inserting the specimen into the reservoir, black wax was painted around the edges of the specimen to minimise current leakage, and the top surface electrical contact was made with Ag paint.

Pore growth was carried out at a constant voltage from 0.5-3V using a Fischione power supply. A typical current was 0.01mA, corresponding to 1000mA cm^{-2} over the "active" cross sectional area (but see below).

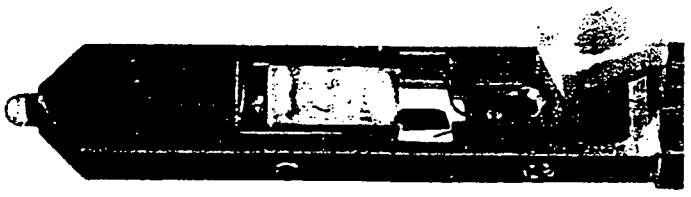

Figure 1. Electrochemical biasing specimen holder. A second (sectioned) reservoir is placed on the holder for illustration.

4. *EX SITU* RESULTS

Figure 3 shows the results of etching *ex situ* (i.e. at 1 atm.). The pores have propagated 250μm from the initial window to the electron transparent region. Cross sectional SEM confirms that etching occurs in the n^+ layer, so the aspect ratio of these pores is 250μm/400nm ~ 600. The pore front is very straight so all pores are propagating at the same speed. Rather than forming the well separated, highly branched pores which have been observed in n-type silicon, the etching process has removed most of the material, leaving behind walls less than 50nm thick. Although pore morphology is known to be a sensitive function of the etching conditions, the morphology observed here is unusual and may be related to the confinement of the pores into a small cross sectional area. The striking light and dark bands in the image were created artificially by modulating the voltage. This technique allows us to mark the pore front at selected times and suggests some exciting possibilities related to the creation of density superlattices. Our films generally show small scale modulations which we believe are due to fluctuations in the current.

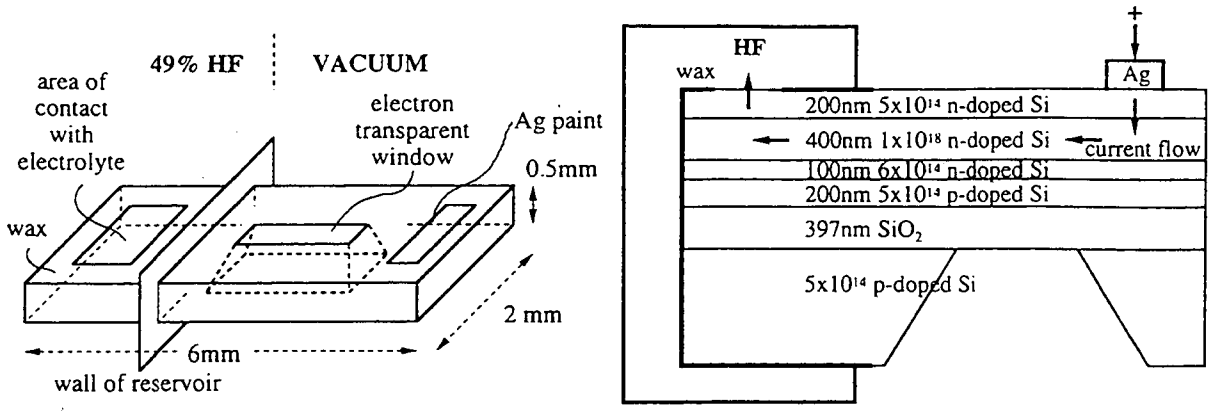

Figure 2. Schematic diagrams showing the overall specimen geometry and details of the layers.

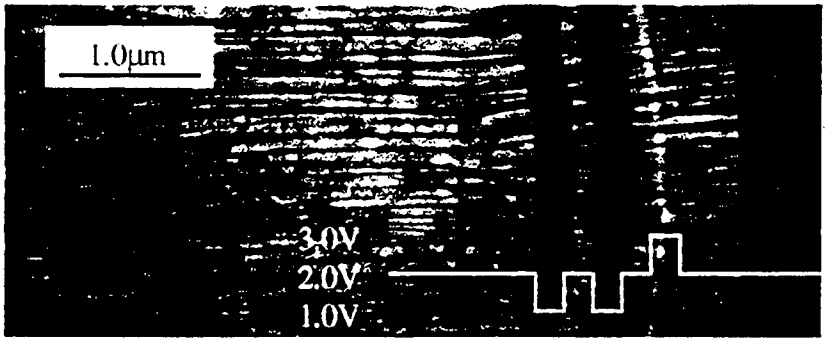

Figure 3. Bright field, plan view image of the pore front after etching *ex situ* in the (100) direction for 32 min. at 2.0V and 0.016mA. Inset is the time-varying voltage which was applied to create the bands of varying porosity. This enables us to calculate etch rate as a function of applied voltage.

We now consider some specimen geometry related issues which have arisen from these *ex situ* experiments. We were initially concerned that pores would not propagate far enough to reach the electron transparent window. Figure 3 shows that this is not a problem, and we have propagated pores as far as 1500μm. Furthermore, I-V curves from specimens etched in the reservoir are identical to those from specimens etched in a large beaker of HF. This suggests that exhaustion of the HF by saturation or slow diffusion of etching products is not limiting the reaction.

Vertical propagation is a problem if it allows the escape of electrolyte. Cross sectional SEM shows that pores do grow vertically, and we see a distinctive cellular morphology in plan view

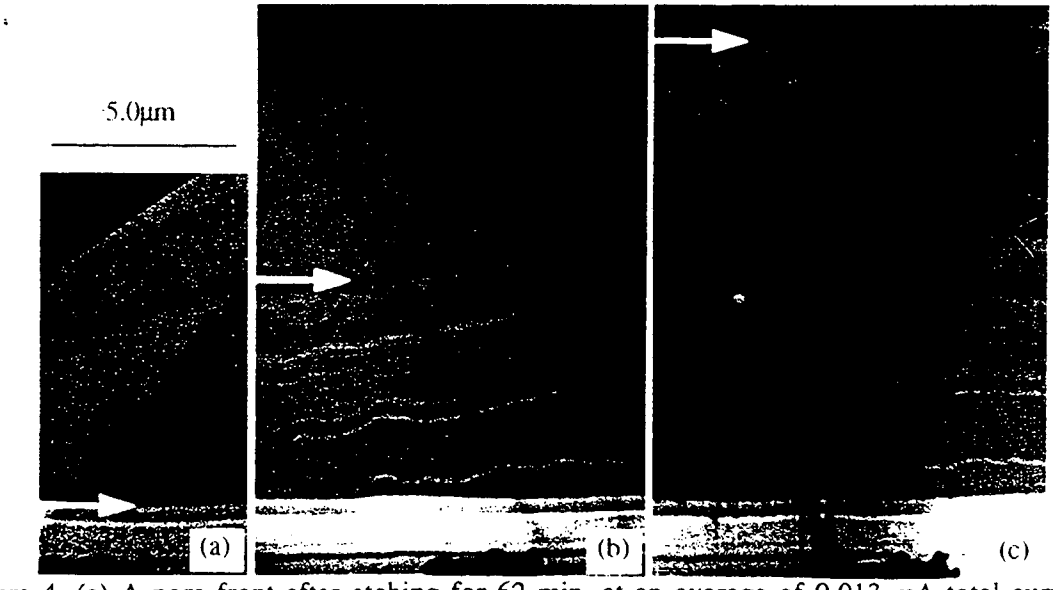

Figure 4. (a) A pore front after etching for 62 min. at an average of 0.013 mA total current. (b) After a further 10 min. 30 s. at 0.007 mA. (c) After a further 10 min. 15s. at 0.010 mA. Between (a) and (b) the pore front has advanced irregularly, probably because the specimen was left overnight in between. However (b) and (c) were carried out within an hour and the pore front at (c) has retained its profile at (b).

when this happens. This actually simplifies the specimen design since it is not necessary to pattern contact windows through the barrier layer to the active layer. However, it is a potential problem in experiments under vacuum. Barrier layers 200 nm thick appear to provide a compromise between containing the HF (*ex situ*) and still allowing reasonable electron transmission. It is possible that replacement of the top layer with a thinner Si_xN_y layer will improve image quality further.

At present, we have not observed pore growth in real time within the microscope, and are working on a reliable vacuum seal between the specimen and the reservoir. However, in figure 4 we show an interesting series of images taken after successive ten minute periods of etching, again *ex situ*. The pore front has propagated at speeds of 10.8 and 10.2 nm s^{-1}, corresponding to a current density of 4.2 mA cm^{-2} (ssuming a porosity of 50%).

5. CONCLUSIONS AND FUTURE DIRECTIONS

We have demonstrated that it is possible to carry out electrochemical etching inside a buried layer in the electron transparent region of a silicon specimen. After further vacuum testing we hope to allow this process to take place within the microscope. We are very excited by the possibility of examining the etching reaction in real time and at moderately high resolution. Our initial objectives are to study the porosity, morphology and etch rate as a function of voltage and doping level, and to observe the process of pore branching. As the voltage increases the system enters the electropolishing régime where material is removed isotropically. We expect to find changes in morphology as this transition point is approached. Another area of interest is the behaviour of the etch rate when the voltage is removed, which could indicate the presence of certain species at the silicon/HF interface. Finally, the flow of current along dislocations can be studied by using partially relaxed Ge_xSi_{1-x}/Si substrates with misfit dislocations at the interfaces.

There are analogous systems for which this type of *in situ* experimentation would prove valuable, such as n-type GaAs, where the pores run in <111>a directions and have triangular or hexagonal cross sections and interesting branching geometry (Ross et al. 1995b). Modifications of the holder and specimen design can extend these experiments further and we are presently fabricating specimens in which we can study the dynamical behaviour of ionic conductors and ferroelectric thin films under an applied field.

We gratefully acknowledge John C. Bean and J. Alex Liddle of AT&T Bell Laboratories, NJ for MBE growth and scanning electron microscopy, respectively, Andrew Wittkower of SOITEC/USA, MA, for kindly providing the SIMOX wafers, and M. L. Tech, CA, for construction of the specimen holder. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Science Division, U. S. Department of Energy under contract DE AC-03-76SF00098, and by the National Science Foundation under grant DMR-9202645.

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